PH06
INVESTIGACIÓN

LIBS in cultural heritage: exploration and identification of objects at underwater archaeological sites

Francisco Javier Fortes **01|** Marina López-Claros **01|** Salvador Guirado **01|** Javier Laserna **01|**

In this work, the capabilities of LIBS technique for the in-situ recognition and identification of materials in real submerged archaeological sites are discussed. A fiber-optics-based remote instrument was designed for the recognition and identification of archeological assets in underwater archaeological shipwrecks. The LIBS prototype featured both single-pulse (SP-LIBS) and multi-pulse excitation (MP-LIBS). The use of multi-pulse excitation allowed an increased laser beam energy (up to 95 mJ) transmitted through the optical fiber. This excitation mode results in an improved performance of the equipment in terms of extended range of analysis (to a depth of 50 m) and a broader variety of samples to be analyzed (i.e., rocks, marble, ceramics and concrete). Parametric studies in the laboratory such as gas flow pressure, beam focal conditions and angle of incidence, among others, were performed to optimize the best conditions for field analysis. The dependence of LIBS signal with the analysis depth was also studied in a real environment (Bahía de Málaga). Ancient artifacts found in the wreck of *Bucentaure* (Cádiz, Spain) and the wreck of San Pedro de Alcántara (Málaga, Spain) have been characterized and identified. Results obtained in these field trials confirmed the capability of remote LIBS for in-situ analysis of underwater archeological samples.

Keywords
Underwater analysis | Archaeology | Laser-induced breakdown spectroscopy | Intervention | LIBS | Underwater archeological heritage | Cultural heritage | Historical heritage |

LIBS en patrimonio cultural: reconocimiento e identificación de objetos en yacimientos arqueológicos sumergidos

Francisco Javier Fortes **01|** Marina López-Claros **01|** Salvador Guirado **01|** Javier Laserna **01|**

En este trabajo se discutirán las capacidades de la técnica LIBS para el reconocimiento e identificación in situ de materiales sumergidos en yacimientos arqueológicos reales. Se ha diseñado un instrumento remoto basado en fibra óptica que permite el reconocimiento e identificación de objetos en este tipo de escenarios. El prototipo desarrollado por la U. de Málaga es capaz de trabajar en dos configuraciones, pulso-simple convencional (SP-LIBS) y excitación multi-pulso (MP-LIBS). El uso de una configuración de multi-pulso permitió aumentar la cantidad de radiación láser (hasta 95 mJ) que puede ser transmitida a través de un cable de fibra óptica. Como consecuencia, se produce una mejora de las prestaciones del equipo, sobre todo en términos de rango de análisis (hasta una profundidad de 50 metros) y variedad de muestras que pueden ser analizadas (por ejemplo, rocas, cerámica, mármol y hormigón). Previamente, se han realizado estudios de parametrización en laboratorio (presión del gas, condiciones focales, ángulo de incidencia…) para alcanzar las mejores condiciones durante las medidas de campo. La dependencia de la señal LIBS con la profundidad de muestreo se estudió en un escenario real. Por otro lado, se caracterizaron e identificaron los objetos arqueológicos encontrados en el pecio del *Bucentaure* (Cádiz) y el pecio de San Pedro de Alcántara (Málaga). Los resultados obtenidos durante estas campañas de medida confirmaron la adaptabilidad de la técnica al ambiente marino y su potencial para analizar objetos arqueológicos en un yacimiento subacuático.

Palabras clave
Análisis subacuático | Arqueología | Espectroscopía de plasmas inducidos por láser | Intervención en el PH | LIBS | Patrimonio arqueológico subacuático | Patrimonio cultural | Patrimonio histórico |

URL <http://www.iaph.es/phinvestigacion/index.php/phinvestigacion/article/view/140>

01| Departamento de Química Analítica, Universidad de Málaga

Salvo que se indique lo contrario, esta obra está bajo una licencia Reconocimiento -No Comercial- Sin obra Derivada 3.0 España Creative Commons
Documento traducido gracias a la desinteresada colaboración de Morote Traducciones. Artículo publicado inicialmente en español: *ph investigación* n.º 5 (diciembre, 2015)

FORTES, F. J.; LÓPEZ-CLAROS, M.; GUIRADO, S.; LASERNA, J. (2016)
LIBS in cultural heritage: exploration and identification of objects at underwater archaeological sites
ph investigación [en línea], n.º 6, junio de 2016, pp. 25-46
<http://www.iaph.es/phinvestigacion/index.php/phinvestigacion/article/view/140>

INTRODUCTION

At present, the characterisation of underwater cultural heritage has become one of the areas of greatest interest in archaeology (BOWEN, 2009). The main reason is the amount of historical information contained in these sunken archaeological remains, not only at the bottom of seas and oceans where the majority of these sites are found, but also at other locations such as rivers, lakes and swamps (BONIFACIO, 2008; LEÓN AMORES, 2009). More specifically, the Mediterranean Sea is home to a large amount of archaeological remains as a result of the storms, accidents and naval battles it has witnessed since Antiquity. In particular, the coast of Andalusia can be considered a privileged enclave where a multitude of sites of archaeological interest can be found. Given its geographical location, the Mediterranean has been utilised throughout history as an area of transit by many commercial and military routes - hence the great interest aroused by maritime archaeology.

Each archaeological site is a valuable source of historical information. We must point out that the reality of an underwater site tends to differ considerably from the ideal image initially presented by a shipwreck. Normally the remains from the site cannot even be distinguished from their surroundings since these remains end up becoming integrated into the landscape due to the effects of time and continuous sediment deposition. The discovery of pieces such as amphorae and cannons, in their archaeological context, could give indications of the age of the shipwreck as well as where it came from. It is essential to study, protect and preserve sunken properties given the constant aggressions they are subjected to. Classic analytical techniques generally require that the piece be taken to the laboratory in order to study its composition. This, however, is not always possible.

Sometimes the object cannot be removed from its site because of logistical issues, such as its size for example. Other times, the reason may be due to legislation or may put the object's integrity in jeopardy. The materials present at the site are in a chemical balance with their surroundings, thus preventing their deterioration. After being removed, the pieces out of water begin to oxidise as a result of the oxygen in the air and the electrolytes that may be occluded in their interior. Preventing this process is complex, costly and could take several months. Thus, the in situ analysis of objects tends to be the only alternative in many cases. Furthermore, but not less important, it is necessary to keep in mind that the position of the object in the context of the site can provide us with information about it. This information would be lost if the object was removed from its environment. Therefore, the United Nations Educational, Scientific and Cultural Organization (UNESCO), under the Convention for the

protection of underwater cultural heritage, states that the preservation in situ of cultural heritage shall be considered as "the first option before allowing or engaging in any activities directed at this heritage" (CONVENTION, 2001).

Despite this principle, not many analytical techniques are available for conducting chemical analyses in situ on underwater archaeological objects. In fact, only those based on laser technology are capable of addressing this challenge. One of these techniques has been Raman spectroscopy, which has been used to determine the chemical composition of minerals present on the sea floor (WHITE; DUNK; PELTZER et al., 2006). Laser-induced fluorescence (LIF) has also been utilised in the development of portable instrumentation for taking underwater measurements (FANTONI; BARBINI; COLAO et al., 2006). However, although the Raman and LIF technologies can be applied in this field, they do not provide atomic information.

Now, laser-induced breakdown spectroscopy (LIBS) provides a new solution to this problem (FORTES; LASERNA, 2010; FORTES; MOROS; LUCENA et al., 2013). The development of technology has helped this technique to become, over recent years, a tool with growing applications for the study and preservation of historical heritage (FORTES; CORTÉS; SIMÓN et al., 2005; GIAKOUMAKI; MELESSANAKI; ANGLOS, 2007; FORTES; CUÑAT; CABALÍN et al., 2007). The LIBS technique reunites practically all of the desired conditions for this type of application, including atomic, multi-elemental information, an unlimited range of materials that can be analysed and real-time results without the need to prepare the sample beforehand. Additionally, both the basic fundamentals of underwater LIBS measurements as well as the measurement principles, instrumentation and most appropriate methodologies have been described in the literature (LAZIC; LASERNA; JOVICEVIC, 2013a; LAZIC; LASERNA; JOVICEVIC, 2013b). The analysis of liquids using LIBS was evaluated for the first time in 1984 (CREMERS; RADZIEMSKI; LOREE, 1984).

The processes resulting from the laser-liquid interaction lead to the emission of a very weak plasma that, while still useful for analytical purposes, presents difficulties associated with the instability of the emission (CHARFI; HARITH, 2002). The analytical capacity of the technique for the analysis of underwater materials improves considerably with double-pulse LIBS systems (DE GIACOMO; DELL'AGLIO; COLAO et al., 2004; DE GIACOMO; DELL'AGLIO; DE PASCALE et al., 2007). With this methodology, emission efficiency substantially improves and the signal is stabilised, achieving an accuracy that leaves a margin of error of only 10-15%. This configuration has been applied for the semi-quantitative analysis

FORTES, F. J.; LÓPEZ-CLAROS, M.; GUIRADO, S.; LASERNA, J. (2016)
LIBS in cultural heritage: exploration and identification of objects at underwater archaeological sites
ph investigación [en línea], n.º 6, junio de 2016, pp. 25-46
<http://www.iaph.es/phinvestigacion/index.php/phinvestigacion/article/view/140>

of solid samples and marine sediment. Recently, the capacity of LIBS for the underwater analysis of metal alloys (iron, bronzes and precious alloys) and non-metal samples (rock and wood) has been demonstrated (LAZIC; COLAO; FANTONI et al., 2005). Thus, the analysis of metallic materials is of vital importance since it allows for the identification of the primary metallic constituents in iron, copper, gold and silver alloys, as well as the detection of trace and minor elements of interest for the clarification of sample origins and the identification of manufacturing processes.

However, all of the studies described to date on underwater materials have been carried out in the laboratory. This research study intends to describe the activities conducted as part of the AQUALAS Project, stemming from the need to solve a well-defined problem: chemically characterising the materials present at an underwater archaeological site without removing them from their original location. The following objectives are posed:

> Broaden the range of application of the LIBS technique for the inspection, identification and diagnosis of properties located in underwater archaeological sites.

> Develop a portable underwater material analysis system adapted to the marine environment.

> Study the conditions necessary for the identification and preservation of underwater cultural heritage.

In 2012, the laser laboratory at the University of Málaga published the first underwater LIBS analysis on solid samples (GUIRADO; FORTES; LAZIC et al., 2012). The system consisted of a main unit (where laser-fibre coupling takes place) and a submersible probe, connected by a 40-metre long cord. The prototype was controlled from the deck of a boat while a professional diver operated the submersible LIBS probe. The test was carried out on the Mediterranean Sea at a maximum depth of 30 metres. The system introduces a coaxial flow of gas that eliminates the water from the surface of the sample and generates a solid-gas interface which facilitates the LIBS analysis under water. Although the results were quite satisfactory, the analyses were practically restricted to metallic samples. Subsequently, the same authors considered the possibility of utilising a multi-pulse configuration or, in other words, a sequence of successive laser pulses (GUIRADO; FORTES; CABALÍN et al., 2014). With this configuration, the unit's performance improved in terms of a) laser energy transmitted with the fibre optic, b) range of analysis and c) variety of samples that can be analysed (for example marble, ceramic, concrete...).

FORTES, F. J.; LÓPEZ-CLAROS, M.; GUIRADO, S.; LASERNA, J. (2016)
LIBS in cultural heritage: exploration and identification of objects at underwater archaeological sites
ph investigación [en línea], n.º 6, junio de 2016, pp. 25-46
<http://www.iaph.es/phinvestigacion/index.php/phinvestigacion/article/view/140>

These improvements made to the prototype have made interventions on underwater archaeological sites possible, such as the shipwreck Bucentaure (GUIRADO; FORTES; LASERNA, 2015) and the shipwreck San Pedro de Alcántara (July, 2015). Throughout this article we will discuss the capacities of the technique for the exploration and identification in situ of underwater materials at real archaeological sites.

MATERIALS AND METHODS

Instrumentation

This section presents a novel instrument that has been specially designed for the remote chemical analysis of underwater materials. This system can be configured for either the conventional single-pulse (SP-LIBS) or the multi-pulse (MP-LIBS). The MP-LIBS configuration makes it possible to introduce greater laser radiation using the fibre optic. Thus, the maximum input energy into the fibre was 95 mJ/pulse that, together with a transmission of 74%, allowed for an energy output of 70 mJ/pulse to be met. This improved instrument performance in terms of energy transmitted via the fibre, range of analysis (up to 50 metres deep) and the variety of samples that could be analysed (marble, ceramic, concrete, rocks...).

The prototype consists of two well-defined parts: a sampling probe and a main unit, interconnected with a 50-metre-long cord. Image 1 gives a general view of the instrument. The main unit contains the optical module where laser-fibre coupling takes place, the data acquisition module and the laser power supply. The total weight of the instrument amounts to about 150 kg and it measures 81x86x126 cm.

The optical module consists of a methacrylate structure specifically adapted to prevent the deposit of marine aerosol on the system's optical components. This module also contains the laser beam source as well as all of the optical components to carry out both laser-fibre coupling and the detection of plasma from the surface of the sample.

The laser beam is transmitted through 55 metres of fibre optic protected inside of a cord that connects the analysis probe with the optical module. At the very end of the fibre optic, the laser beam is focused on the surface of the material using an optical system which is incorporated into the interior of the LIBS analysis probe. The cord also provides a constant flow of gas to the inside of the probe, eliminating the water from the surface of the material and creating a gas-solid interface which facilitates the LIBS analysis under water.

Image 01 |
A general view of the AQUALAS instrument. Photo: all of the images displayed in this article are from UMA LASERLAB unless indicated otherwise

FORTES, F. J.; LÓPEZ-CLAROS, M.; GUIRADO, S.; LASERNA, J. (2016)
LIBS in cultural heritage: exploration and identification of objects at underwater archaeological sites
ph investigación [en línea], n.º 6, junio de 2016, pp. 25-46
<http://www.iaph.es/phinvestigacion/index.php/phinvestigacion/article/view/140>

Once the plasma has been generated on the surface of the material, the light is transmitted via the same fibre optic to return to the optical module where it is guided towards the data acquisition module through an optical collection system. The data acquisition module, installed on the main unit, features a spectrometer, a video converter and a computer. A pulse and delay generator externally controls the system.

The Czerny-Turner spectrometer has a diffraction grating of 1200 lines/mm. With this configuration a spectral resolution of 0.1-0.2 nm/pixel is obtained in addition to a spectral range of 300-550 nm. The time-space acquisition conditions were optimised to obtain the best signal-noise ratio in the LIBS signal.

The tool also features an auxiliary module for its full autonomy during field studies. This module contains an air compressor, a current stabiliser and an external current generator which provides the tool with seven hours of work autonomy.

Materials

In order to evaluate the capacities of the technique and fine-tune the remote LIBS tool, a series of samples were analysed in the laboratory. This collection of objects included ceramic material as well as metal alloys; the majority of the pieces presented a high degree of corrosion and surface roughness.

These samples are summarised in table 1. The experiments were conducted inside a 100-litre tank with water taken directly from the Mediterranean Sea so that the laboratory measurements would resemble (as much as possible) the conditions of a real marine-environment analysis.

In the second phase, in order to demonstrate the potential of the technique, measurement campaigns were designed in real scenarios of interest to the investigation of Andalusian underwater archaeological heritage. Thus, the remains from the Bucentaure (Cádiz, Spain) and the shipwreck of San Pedro de Alcántara (Málaga, Spain) were analysed at depths of 17 and 10 metres, respectively.

In table 2 the samples analysed during the measurement campaigns conducted at these two archaeological sites are described. During the archaeological prospecting work on the shipwreck of San Pedro de Alcántara, the chemical composition of samples of sheathing from different shipwrecks was also analysed.

A description of these samples is summarised in table 3.

Sample	Material	Sample description
#1	Ceramic	Archaeologial ceramics with calcareous concretion
#2	Ceramic	Archaeologial ceramics with ferrous concretion
#3	Iron	Archaeological iron piece
#4	Bronze	Bronze sheet
#5	Bronze	Archaeological bronze
#6	Bronze	Leaded bronze
#7	Bronze	Certified sample bronze (79% Cu, 8% Pb, 7% Sn, 6% Zn)

Table 01 |
Samples analysed in the laboratory as well as during the tests conducted on the Mediterranean Sea (Málaga, Spain) in 2010

Sample	Shipwreck	Material	Sample description
#8	*Bucentaure*	Iron	Piece of iron with calcareous concretion
#9	*Bucentaure*	Iron	Metal box for storing items of jewelry
#10	*Bucentaure*	Iron	Iron cannon with high concretion degree
#11	*Bucentaure*	Copper	copper object with calcareous concretion
#12	*Bucentaure*	Lead	Pieza de plomo
#13	San Pedro Alcántara	Ceramic	Decorated ceramics
#14	San Pedro Alcántara	Ceramic	Ceramic shard indeterminately
#15	San Pedro Alcántara	Ceramic	Fragment of a possible ceramic container
#16	San Pedro Alcántara	Iron	Cannonball
#17	San Pedro Alcántara	Iron	Iron cannon
#18	San Pedro Alcántara	Iron	Iron cannon
#19	San Pedro Alcántara	Iron	Iron piece indeterminately
#20	San Pedro Alcántara	Bronze	Fragment of a buckle
#21	San Pedro Alcántara	Copper	Copper button
#22	San Pedro Alcántara	Copper	Copper fragment indeterminately

Table 02 |
Samples analysed during the tests carried out on the shipwreck *Bucentaure* (Cádiz, Spain) and the shipwreck San Pedro de Alcántara (Málaga, Spain)

sample	Shipwreck	Origin	Sample description
#23	*Bucentaure*	Francia	Cooper sheathing
#24	*Bucentaure*	Francia	Cooper sheathing
#25	*Bajo S. Sebastián*	España	Cooper sheathing
#26	*Bajo S. Sebastián*	España	Cooper sheathing
#27	Delta II	Italia	Cooper sheathing
#28	Delta II	Italia	Cooper sheathing

Table 03 |
Samples of sheathing analysed during the tests carried out on the shipwreck San Pedro de Alcántara (Málaga, Spain)

FORTES, F. J.; LÓPEZ-CLAROS, M.; GUIRADO, S.; LASERNA, J. (2016)
LIBS in cultural heritage: exploration and identification of objects at underwater archaeological sites
ph investigación [en línea], n.º 6, junio de 2016, pp. 25-46
<http://www.iaph.es/phinvestigacion/index.php/phinvestigacion/article/view/140>

RESULTS AND DISCUSSION

Optimisation of experimental parameters in remote LIBS analysis underwater

A) Effect of the probe operational parameters on the LIBS signal

To achieve the best results provided by the tool, those parameters capable of affecting the quality of the LIBS signal were optimised in the laboratory, such as the lens-sample distance and the angle of incidence of the laser radiation. The parameterisation studies were conducted utilising a certified bronze sample inside of a water tank.

The submersible probe consists of an opening with a 2 mm diameter whose position must be adjusted in order to reach the optimal focus conditions. The probe must be in direct contact with the surface of the sample. In this first test, He was utilised at a pressure of 2 bars as a protective gas. The same sampling protocol was always employed in order to ensure the exactness and precision of the measurements. Each analysis point is the result of averaging 5 measurements, each of which examined with 25 laser pulses. The measurement value is obtained by averaging the last 15 pulses of the series after considering the first 10 cleaning pulses. Image 2 shows the intensity of the Cu (I) 521.96 nm signal as a function of the working distance. A distance of 0 mm means that the sample is located at the focal point of the lens. We can observe how the net intensity of copper reaches its maximum value when the beam is focused 0.5 mm above the surface of the sample (+0.5 mm). Similar behaviour is observed when the focal point is situated 0.5 mm below the surface of the sample (-0.5 mm). In both cases, the LIBS signal quickly decreases as the distance increases since the amount of energy deposited on the surface of the sample is reduced in terms of radiant exposure (J/cm^2). In other words, the same energy per pulse is applied to an increasingly larger surface area as the beam goes out of focus. The operating range is narrow as a consequence of the short focal distance (35 mm) required to focus the laser from the output end of the fibre optic. In light of these results, the working distance was set to 0.5 mm over the surface of the sample.

The impact of the angle of incidence of the laser with regard to the surface of the sample was a parameter that needed to be considered bearing in mind the extreme conditions the diver was subjected to on account of the sea currents. Image 3 shows the impact of the angle of incidence of the laser radiation on the LIBS signal of a bronze sample. As can be observed, the maximum signal is reached when the probe is placed practically normal to the surface (0-10º). When the intensity of the copper is normalised to the background of the spectrum, the LIBS

FORTES, F. J.; LÓPEZ-CLAROS, M.; GUIRADO, S.; LASERNA, J. (2016)
LIBS in cultural heritage: exploration and identification of objects at underwater archaeological sites
ph investigación [en línea], n.º 6, junio de 2016, pp. 25-46
<http://www.iaph.es/phinvestigacion/index.php/phinvestigacion/article/view/140>

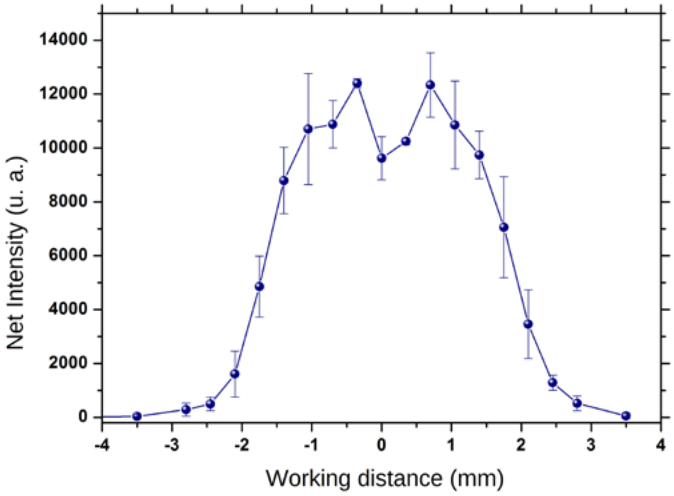


Image 02 |
Intensity of Cu (I) 521.96 nm according to the working distance

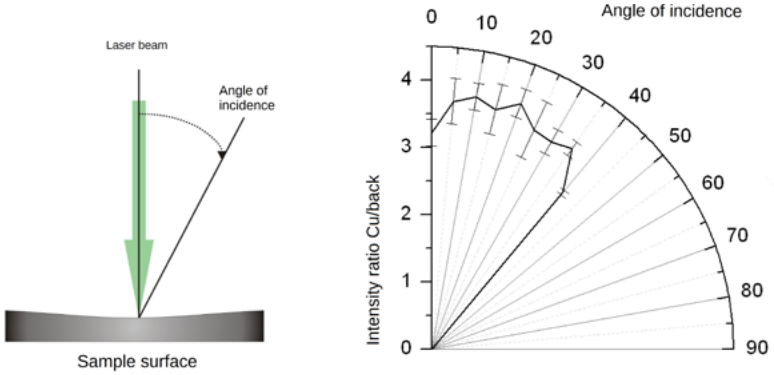


Image 03 |
Relationship between the angle of incidence between the laser radiation and the surface of the sample and the Cu/background intensity

response remains nearly constant in a range between 0º and 40º. However, no signal is observed beyond this angle due to the difficulty involved in collecting the light from plasma under those geometric conditions.

B) Protective gases

The use of a protective gas or a purge gas is key to preventing the entry of water into the inside of the analysis probe. The great diminishing effect that water has on the radiation of 1064 nm would prevent a sufficient amount of energy from being deposited onto the analysis spot. At the same time it hinders the deposit of particles from the sample on the focusing lens. The flow of gas from the auxiliary module travels via the cord and is expelled outside through a hole at the tip of the probe. This flow of gas displaces the water on the surface of the sample and creates a solid-gas interface, thus facilitating the LIBS analysis under water. In this way, in comparison with a solid-

FORTES, F. J.; LÓPEZ-CLAROS, M.; GUIRADO, S.; LASERNA, J. (2016)
LIBS in cultural heritage: exploration and identification of objects at underwater archaeological sites
ph investigación [en línea], n.º 6, junio de 2016, pp. 25-46
<http://www.iaph.es/phinvestigacion/index.php/phinvestigacion/article/view/140>

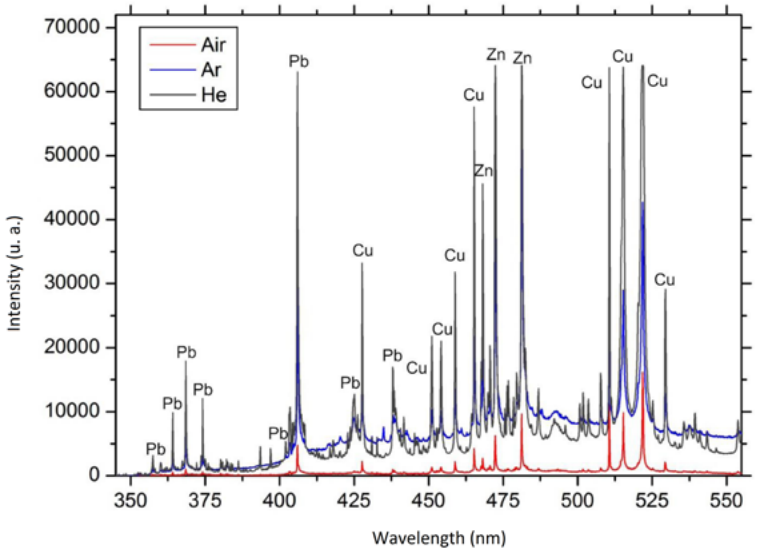


Image 04 |
LIBS spectra (from a sample of bronze) obtained from an environment of air, helium and argon. The main emission lines are labelled on the spectrum

liquid interface, ablation efficiency is improved since the loss of energy which would cause the liquid to heat is prevented.

Additionally, greater plasma emission occurs as a result of the increase in both the temperature and its electron density. This is due to the collisions that occur with the surrounding gas and the ablated material, the electrons and the different species (excited or not) present in the plume. Different gases (Ar, He and air) were evaluated during the analysis of a certified bronze sample. The results are shown in Image 4. As it can observe, the most intense signal was given by He. Nonetheless, no additional information was observed regarding the composition of the sample in comparison with the results obtained using air. Thus, seeing as the air is easily obtained using the portable compressor as well as far less costly, it is logical to utilise this gas for the routine analysis. The use of helium or argon may be useful in some specific applications where increasing signal sensitivity is necessary, for instance for the quantitative analysis of minor elements or during the analysis of ceramic material.

In order to prevent air from entering the inside of the analysis probe, the differential pressure (ΔP) between the interior and exterior of the probe must be greater than 1 bar. Image 5 shows the impact of ΔP on the LIBS signal of Cu (521.96 nm), Pb (405.89 nm) and the background. The intensity of the signal is practically constant when ΔP is among 1 and 3 bars. When ΔP presented higher values, an increase in both the LIBS signal and the background was observed. This point is especially interesting when working at great depths at the bottom of the sea. Additionally, the accuracy of the results was quite satisfactory and the values obtained for the relative standard deviation were among 8-15 %.

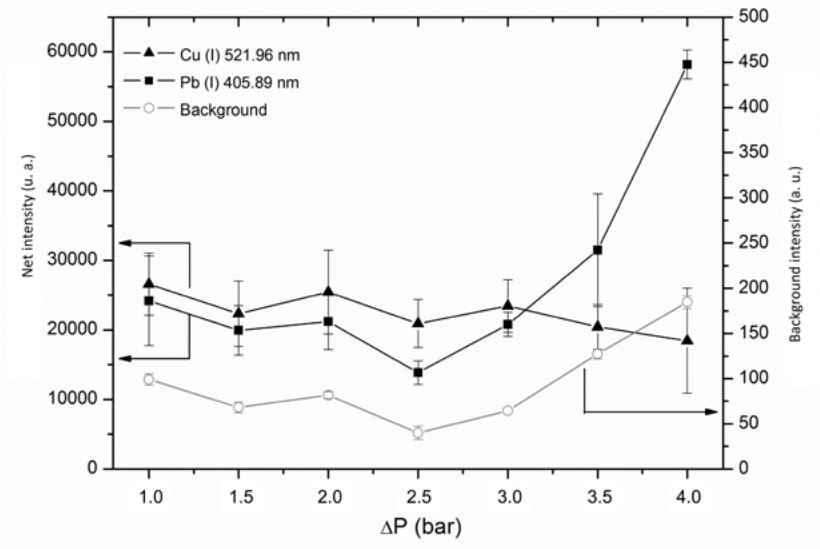


Image 05 |
Impact of the differential pressure (ΔP) –between the interior and exterior of the probe– on the LIBS signal of Cu (521.96 nm), Pb (405.89 nm) and the background intensity

Underwater chemical characterisation of ceramic objects

The effect of sea water on underwater materials typically results in the deposit of sediment on the surface of the sample. This effect is more severe with metals, even causing oxidation of the object. In underwater archaeology objects must be inspected in situ, especially those materials that present a high degree of surface oxidation. Ceramic materials (amphorae, for example) discovered at archaeological sites are usually found covered by several types of deposits: calcareous and ferrous. In order to demonstrate the capacity of the new tool concerning the underwater chemical characterisation of ceramic objects, several samples presenting these two types of deposits were analysed in the laboratory. The samples were submerged in a water tank in order to simulate real conditions. Image 6 shows the LIBS spectra obtained in each case. Calcareous deposits tend to appear as a heterogeneous, white layer only a few millimetres thick. Its spectral fingerprint corresponds to Ca, Mg and traces of Sr. It must be mentioned that both Mg and Sr tend to replace Ca in calcium carbonate structures. The Fe and Sr emission lines detected around 405 nm could be utilised for the detection of low concentrations of these elements as they are found on an interference-free spectral region of other elements. In addition, the build-up of iron also presents other minor elements such as Ca and Mg, attributed to the build-up of sediment on the oxidised surface of the material. Moreover, due to the heterogeneous nature and the porosity of these materials, we observed an increase in the pulse-pulse fluctuation of the signal measured.

The inherent porosity presented by ceramics favours the obstruction of water in their structures. As was described earlier, the cord directs

FORTES, F. J.; LÓPEZ-CLAROS, M.; GUIRADO, S.; LASERNA, J. (2016)
LIBS in cultural heritage: exploration and identification of objects at underwater archaeological sites
ph investigación [en línea], n.º 6, junio de 2016, pp. 25-46
<http://www.iaph.es/phinvestigacion/index.php/phinvestigacion/article/view/140>

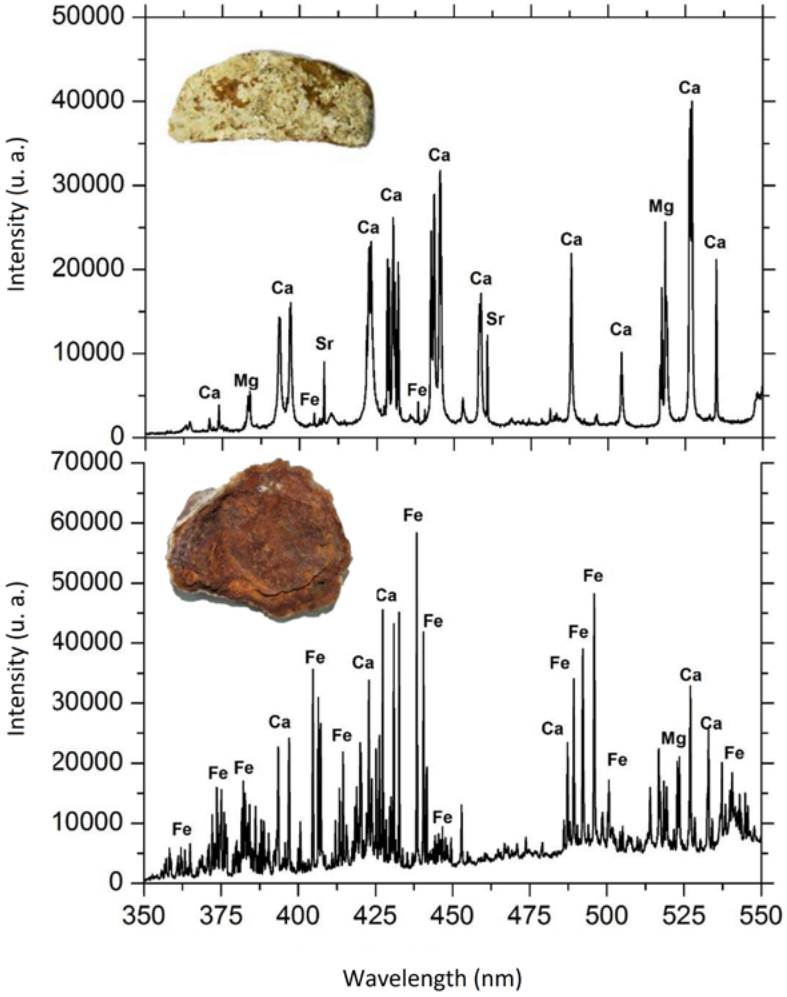


Image 06 |
LIBS spectra of A) calcareous deposit and B) ferrous deposit on a ceramic sample. The main emission lines are labelled on the spectrum

the supply of gas in the probe to remove the water from the surface of the material and create a gas-sample interface that improves ablation efficiency. Image 7, obtained from the literature (GUIRADO; FORTES; LASERNA, 2015), presents the impact of air pressure on the LIBS signal of our ceramic sample. ΔP is the differential pressure between the interior and exterior of the probe. This differential pressure must never be less than 1 in order to correctly prevent water from entering the probe. As we can observe on the graph, while the Ca signal disappears after 25 laser pulses at 1 bar, the intensity of the emission line disappears after almost 60 pulses when the ΔP is increased to 2 and 3 bars. When ΔP = 4 bars, however, the signal is maintained during much more time. This is due to the fact that water molecules are evacuated more efficiently at higher ΔP values, thus facilitating the analysis and consequently the increase in the LIBS signal. In order to improve the chemical characterisation of ceramic materials during a measurement campaign in a real environment conditions, the differential pressure must be set at its maximum value: 5 bars.

FORTES, F. J.; LÓPEZ-CLAROS, M.; GUIRADO, S.; LASERNA, J. (2016)
LIBS in cultural heritage: exploration and identification of objects at underwater archaeological sites
ph investigación [en línea], n.º 6, junio de 2016, pp. 25-46
<http://www.iaph.es/phinvestigacion/index.php/phinvestigacion/article/view/140>

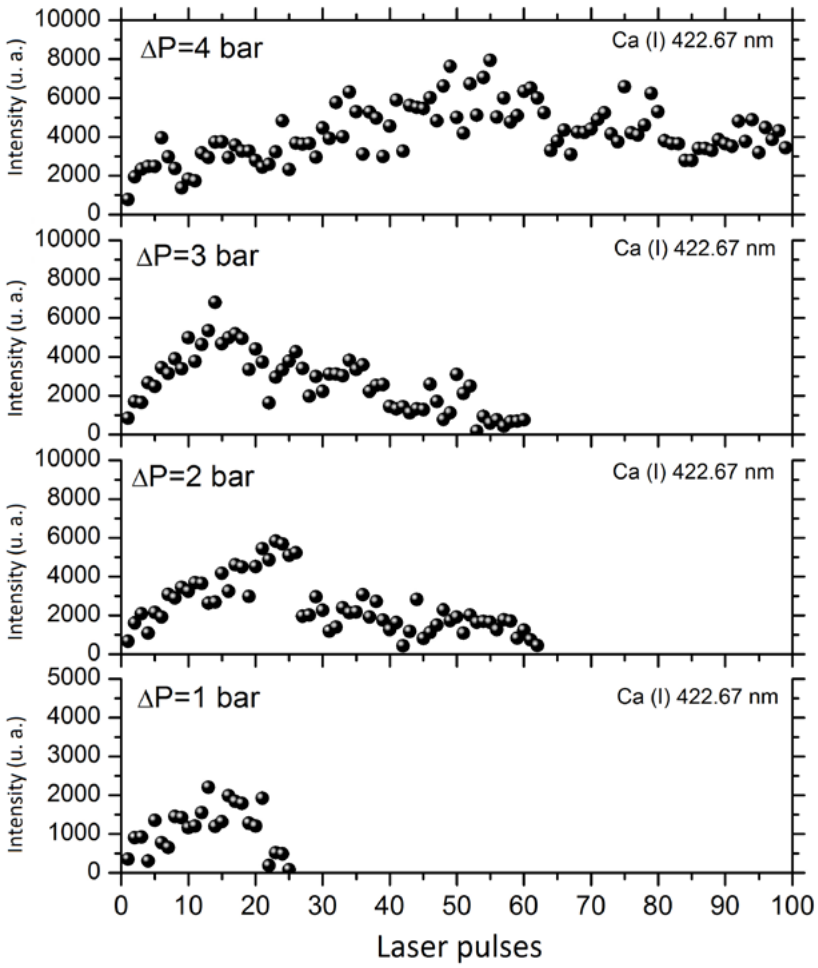


Image 07 |
Impact of air pressure on the intensity of the Ca (I) 422.67 nm signal. ΔP is the differential pressure between the interior and exterior of the analysis probe

Exploration and identification of materials at underwater archaeological sites

The prototype, installed aboard a boat, was controlled by the scientific team while a professional diver operated the analysis probe on the sea floor. The diver was equipped with an audio and video system that allowed for communication with the operators on the boat deck. Furthermore, an assistant diver with a submersible video camera recorded all of the events from the field test. The auxiliary module additionally offered total energy autonomy to the remote LIBS tool.

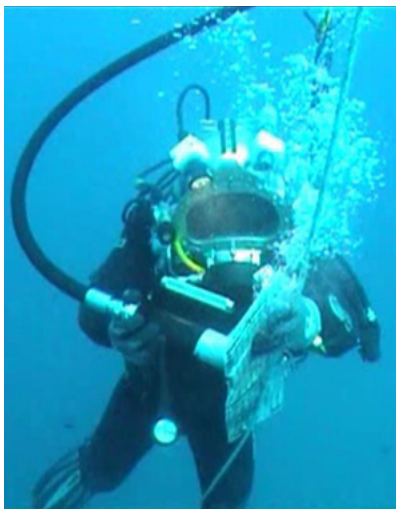
A) Impact of immersion depth on the LIBS signal

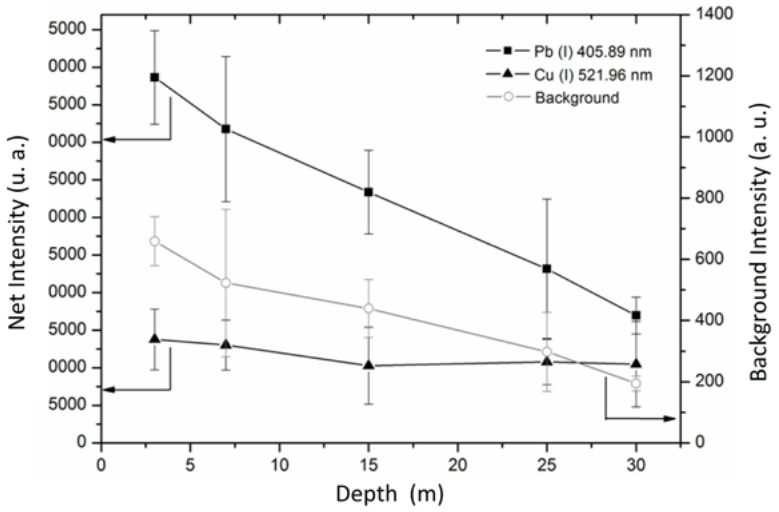
A preliminary test conducted on the Mediterranean Sea in 2010 evaluated the impact of immersion depth on the LIBS signal. In order to reach a depth of 30-35 metres, the boat was anchored approximately a mile off the coast of the Bay of Málaga. At the maximum working depth

FORTES, F. J.; LÓPEZ-CLAROS, M.; GUIRADO, S.; LASERNA, J. (2016)
LIBS in cultural heritage: exploration and identification of objects at underwater archaeological sites
ph investigación [en línea], n.º 6, junio de 2016, pp. 25-46
<http://www.iaph.es/phinvestigacion/index.php/phinvestigacion/article/view/140>

(30 metres), the pressure underwater is 4 bars. To ensure a ΔP greater than 1 bar and thus prevent water from entering the probe, air pressure at the tool's point of entry was set to 5 bars. For this study, a leaded bronze was analysed at different depths: 3, 7, 15, 25 and 30 m. The LIBS signal of Pb (I) 405.89 nm and Cu (I) 521.96 nm was measured according to the immersion depth. The results of this study carried out by GUIRADO; FORTES; LAZIC; LASERNA, 2012 are presented in Image 8. We can observe that the Pb LIBS signal progressively decreased as the depth increased, while the Cu signal remained practically the same throughout the range of depth. This distinct behaviour of Cu and Pb with the immersion depth was attributed to a matrix effect; this means that preferential ablation or fractionation of some species can occur in the laser-induced plasma. In fact, given the temporal width (7 ns) and the wavelength (1064 nm) of the laser pulse, this effect is even more pronounced. On the scale of nano-seconds, the interaction between the laser pulse and the transition states of the elements in the plume could also evaporate material on the surface of the sample. For this reason, the variation observed in the LIBS signal could be attributed to a different volatilisation rate or atomisation process for Pb (Latent heat: 862 J/g; Boiling point: 1740ºC) and Cu (Latent heat: 4790 J/g; Boiling point: 2595ºC) in the plume. This effect, which is very well documented for copper alloys, is related to plasma shielding processes and, in this case, said parameter has been found to be associated with ΔP. Thus, the behaviour of the Pb signal with immersion depth could be attributed to the different values of ΔP, as it is the only parameter that changes during the experiment. As was mentioned at the beginning, the supply pressure was 5 bars and, consequently, the ΔP falls from 4 bars to 1 bar as immersion depth increases. When ΔP presented the highest values (3 m deep, ΔP = 4 bars), the plasma is more confined to the surface of the sample. Therefore, the number of species located in the plasma per

Image 08 |
A diver working at a depth of 30 metres. Image taken during the measurement campaign in the Bay of Málaga; on the right, impact of immersion depth on the LIBS signal





FORTES, F. J.; LÓPEZ-CLAROS, M.; GUIRADO, S.; LASERNA, J. (2016)
LIBS in cultural heritage: exploration and identification of objects at underwater archaeological sites
ph investigación [en línea], n.º 6, junio de 2016, pp. 25-46
<http://www.iaph.es/phinvestigacion/index.php/phinvestigacion/article/view/140>

unit volume is larger, producing a greater plasma shielding effect. As a result, the tail of the pulse invests a large part of its energy into heating the plume, thus meaning that the amount of laser radiation that reaches the surface of the sample is lower. Hence, when the tail of the pulse reaches the surface of the material it will only evaporate the species that have low latent heats of vaporisation, or, the Pb (MARGETIC; PAKULEV; STOCKHAUS, 2000). As a result the plume becomes enriched in Pb, thus increasing the number of species that emit this metal. This is the reason why the intensity of Pb on the LIBS spectrum of the material experiences an increase.

The research carried out thus demonstrates that the LIBS technique offers unique possibilities for the study of underwater archaeological heritage located dozens of metres deep.

B) Spectral characterisation of underwater materials

From an archaeological point of view it is very interesting to have access to a remote LIBS instrument which is capable of examining underwater materials, especially under those circumstances in which the object can not be recognised with the naked eye due to low visibility conditions or an artefact's high degree of corrosion. In this regard, the identification of those discoveries that may be of archaeological value helps to make decisions concerning the convenience (or lack thereof) of removing the sample from its site as well as its subsequent preservation.

In this study measurement campaigns were designed in real scenarios of interest to the investigation of Andalusian underwater archaeological heritage in order to demonstrate the potential of the technique. In the first phase a measurement campaign was organised at a real archaeological site in the Bay of Cádiz. This location was chosen for the multitude of sites present along its coasts. The campaign took place from the 9th to 11th of July 2012 and the work group consisted of members from the laser laboratory at the University of Málaga, a group of archaeologists from the Underwater Archaeology Centre (CAS) (Centro de Arqueología Subacuática), professional divers and technical support personnel from the tugboat 'Obama'. The work was planned in collaboration with the CAS in order to study one of the most important vessels that had sunk off the coast of Andalusia. The remains studied corresponded to the Bucentaure, the flagship of the Franco-Spanish Navy during the Battle of Trafalgar which now rests in the Bay of Cádiz at a depth of 17 metres. We must mention that deposits on the surface of the pieces in analysis areas were removed by qualified professionals who are authorised by the CAS and followed standard procedures. This minimised the risk of damage to the archaeological remains during their handling. Likewise, the analysis areas were

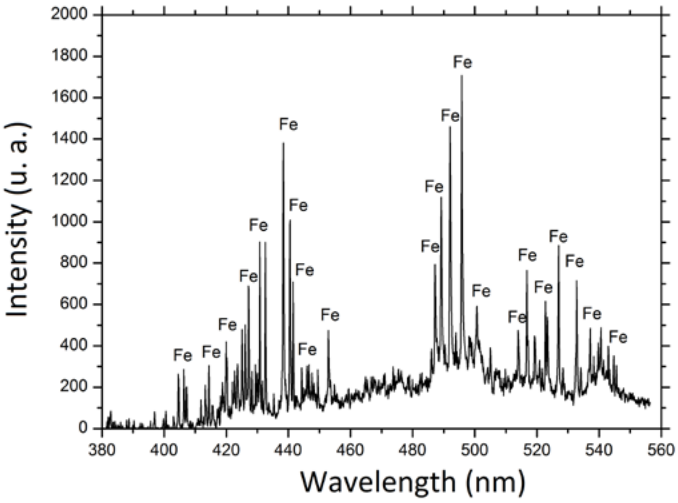
FORTES, F. J.; LÓPEZ-CLAROS, M.; GUIRADO, S.; LASERNA, J. (2016)
LIBS in cultural heritage: exploration and identification of objects at underwater archaeological sites
ph investigación [en línea], n.º 6, junio de 2016, pp. 25-46
<http://www.iaph.es/phinvestigacion/index.php/phinvestigacion/article/view/140>

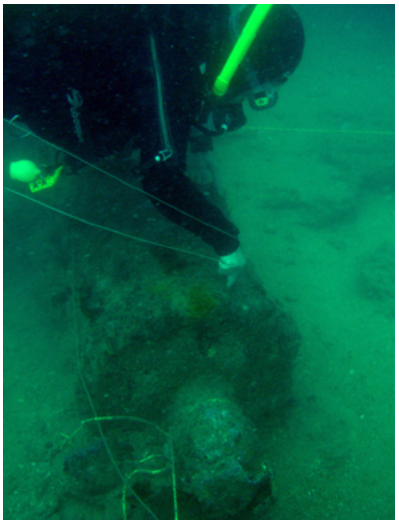
sealed upon completion of the analysis to prevent deterioration of the pieces.

Different objects dating back to the late 18th century and the early 19th century were analysed and identified in situ; these included cannons, a rosary (a metal box for storing the rosary bead necklace) and different metal alloys. These materials were analysed in the 350-550 nm spectral range. These studies applied a flow of gas with a supply pressure of 5 bars. To ensure the reproducibility of the results and achieve a LIBS spectrum representative of each material, the data was obtained by averaging 100 laser pulses in 5 adjacent positions on each sample. Image 9 presents the LIBS spectrum of a cannon composed mainly of Fe and in which the presence of other elements such as Ca and Mg was not detected (typically associated with calcareous and ferrous deposits) once the layer of build-up had been eliminated. The layer of corrosion was eliminated locally; thus, the data obtained by LIBS corresponded exclusively to the original material (image 9A). The relative standard deviation (RSD) of the cannon was 30-40%. During the measurements the ferrous sediment deposited on the surface of the cannon was also analysed. However, the intensity of the LIBS signal was lower on the oxidised area than on the clean surface of the cannon. The variability of the signal was much greater on the corroded surface owing to the heterogeneous nature and the porosity of the material. Image 9B shows a photograph of one of the divers identifying the cannon. Other objects were also inspected such as a rosary and a metallic piece (both identified as iron alloys), a piece of copper and a fragment of lead.

The results obtained were quite satisfactory and allowed, for the first time, for the examination and identification of underwater archaeological materials from the real context of the Chapitel site. Nonetheless, following the measurement campaign carried out at the Bay of Cádiz, some areas to be improved upon were detected in the underwater analyser. For that reason some modifications were made to the analyser, mainly affecting its sturdiness, seal and refrigeration, the sampling probe and data processing. Two experimental campaigns were conducted along the shores of the Mediterranean Sea in order to test out the new improvements that had been made. The instrument was accordingly subjected to conditions which pushed it to the limit in order to demonstrate both its strength and solidity during transport and operation as well as the general improvements made following the campaign in the Bay of Cádiz. These improvements were mainly geared towards facilitating its use and increasing its reliability in hostile environments such as the ocean.

The next step in our investigation was the archaeological exploration with LIBS probing of the underwater site of San Pedro de Alcántara. In



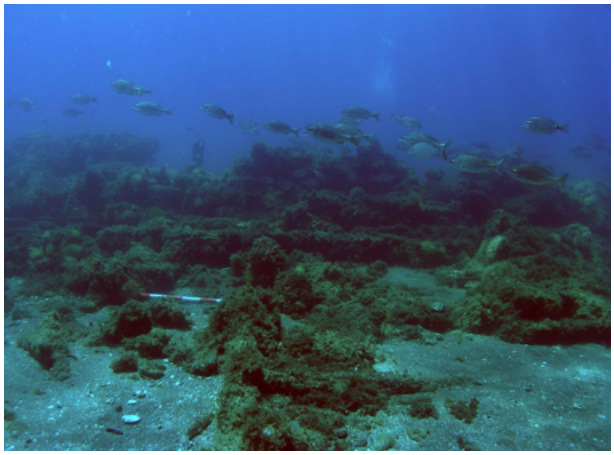


Images 09 (A y B) |
A) LIBS spectrum of an iron cannon recorded during the measurement campaign on the shipwreck *Bucentaure* and B) Photograph taken during examination of the shipwreck. Photo: IAPH Image Archives

this case, the remains of a major vessel were studied in which a strong structural design characteristic of military ships stood out. Measuring approximately 60 m long and about 10-12 m wide, this vessel sits on a floor of sand and debris at a depth that varies between 4 and 7 metres. Image 10 gives a panoramic view of the site. Among the artefacts detected at the site we must emphasise the presence of remains from the ship's ballast, pieces of lumber and pulleys, clothing, buttons, buckles and objects from life aboard the ship and defence of the vessel. The campaign took place from the 20th to 23rd of July 2015 and the work group consisted of members from the laser laboratory at the University of Málaga, a group of archaeologists from the Underwater Archaeology Centre (CAS) (Centro de Arqueología Subacuática), professional divers, an advanced audio and sound technical team and technical support staff from the boat 'Tridacna'. In addition, just as with the shipwreck *Bucentaure*, deposits on the surface of the objects in analysis areas were removed by qualified personnel authorised by the CAS who also inspected the shipwreck and located the position of the materials so that the diver could analyse them with the submersible LIBS probe (image 11). These materials were analysed in the 350-550 nm spectral range.

The sampling and data collection protocol was similar to the protocol described above for the Chapitel site (Cádiz, Spain). With regard to the analytic signal, the presence of self-absorbed resonance lines was not observed. Furthermore, the reproducibility of the spectra obtained underwater was more than acceptable in all cases and presented a variability of less than 10%. Only those samples with a high degree of corrosion presented pulse-pulse fluctuations higher than 10% of the RSD. Image 12 shows the LIBS spectra corresponding to the materials analysed underwater. We can observe that the differences among the

FORTES, F. J.; LÓPEZ-CLAROS, M.; GUIRADO, S.; LASERNA, J. (2016)
LIBS in cultural heritage: exploration and identification of objects at underwater archaeological sites
ph investigación [en línea], n.º 6, junio de 2016, pp. 25-46
<http://www.iaph.es/phinvestigacion/index.php/phinvestigacion/article/view/140>



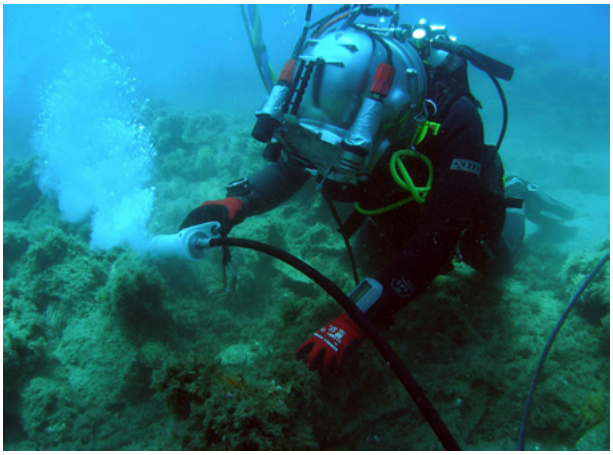


Image 10 |
Panoramic view of the site San Pedro de Alcántara (Málaga, Spain). Photo: IAPH Image Archives

Image 11 |
A diver analysing the shipwreck San Pedro de Alcántara with the LIBS probe. Photo: IAPH Image Archives

materials are significant. Image 12A thus shows that the archaeological ceramic studied is mainly composed of Al, Ca, Fe, Si and Ti; this may be correlated with the chemical composition of a type of clayey material. Image 12B presents the analysis corresponding to the sample catalogued as a copper button, for which Cu was primarily detected, along with traces of Ca and Ti, possibly from calcareous sediment. In the cannonball analysed, Image 12C, Fe was mainly detected, although Mn lines were also identified in its composition. In contrast, only iron was detected in the cannon (image 12D).

One of the studies conducted during the archaeological exploration of the shipwreck San Pedro de Alcántara focused on studying the chemical composition of samples of sheathing from different wreckages.

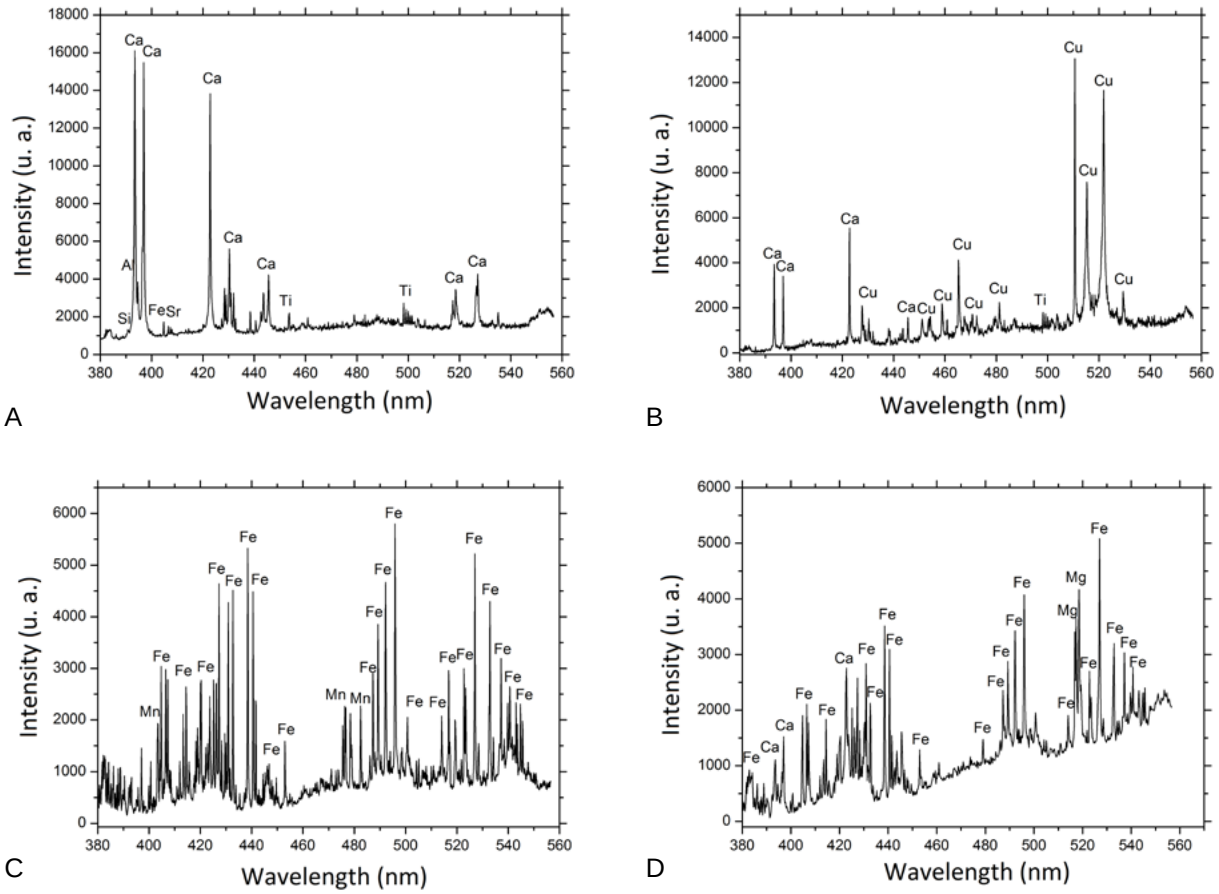
The LIBS analysis is geared towards finding a distinguishing element that makes it possible to correlate the chemical composition with the origin of the shipwreck. The characteristic LIBS spectra are shown in image 13. With regard to the samples from the *Bucentaure*, of French origin, the LIBS spectrum reveals the presence of copper, although in this case it also presents a high concentration of calcium –lines at 393.47 nm, 396.96 nm and 422.79 nm. In the shipwreck *Mercante del bajo de San Sebastián*, of Spanish origin, the LIBS analysis reveals that its sheathing is mainly copper. The shipwreck Delta II is the only Italian wreckage whose sheathing could be analysed. As we can observe in the image, the LIBS spectrum is exclusively composed of lead emission lines, thus ruling out any type of alloy with another chemical element. Although the results obtained could initially establish a correlation between the composition of the material and the origin of the shipwreck, opening up a new line of research, the exclusive analysis of the primary element is not enough to assure this statement, meaning that a more exhaustive study of the minor components is required (BETHENCOURT; BOCALANDRO; ROMERO, 2011).

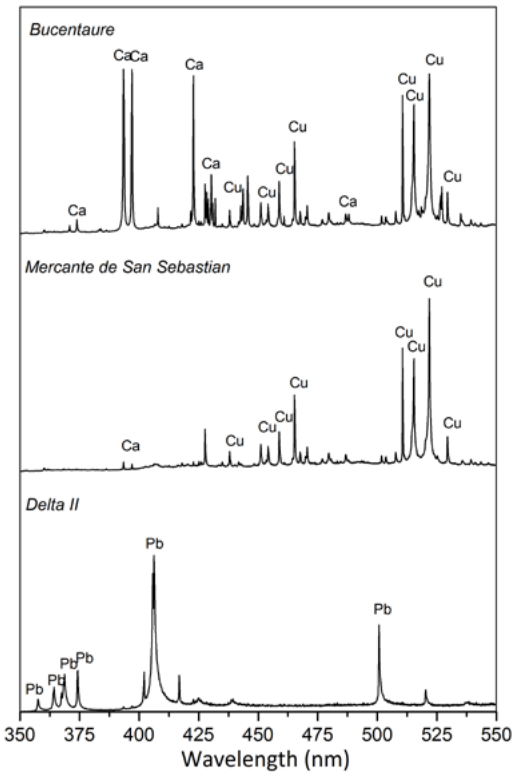
CONCLUSIONS

This research work has demonstrated the potential of laser-induced breakdown spectroscopy (LIBS) for the exploration and identification of archaeological materials at underwater sites. The results obtained during the measurement campaigns confirm the maturity of the technology and its capacity to adapt to the marine environment. Hence, a remote LIBS instrument based on fibre optics and capable of analysing underwater objects at depths of up to 50 metres has been created. The use of a multi-pulse configuration (MP-LIBS) increases the laser radiation transmitted via the fibre optic (74% transmission), thus improving the features of this piece of equipment.

A series of laboratory experiments were conducted with the aim of optimising analysis conditions. In this regard, the LIBS signal is not affected by the angle of incidence in a tolerance range between 0-40º. The use of a purge gas is needed to remove the water from the surface of the sample and generate a solid-gas interface that improves ablation efficiency. The differential pressure must be at least 1 bar in

Image 12 |
Characteristic LIBS spectra of some materials analysed at the site San Pedro de Alcántara: A) ceramic B) copper button C) cannonball and D) iron cannon





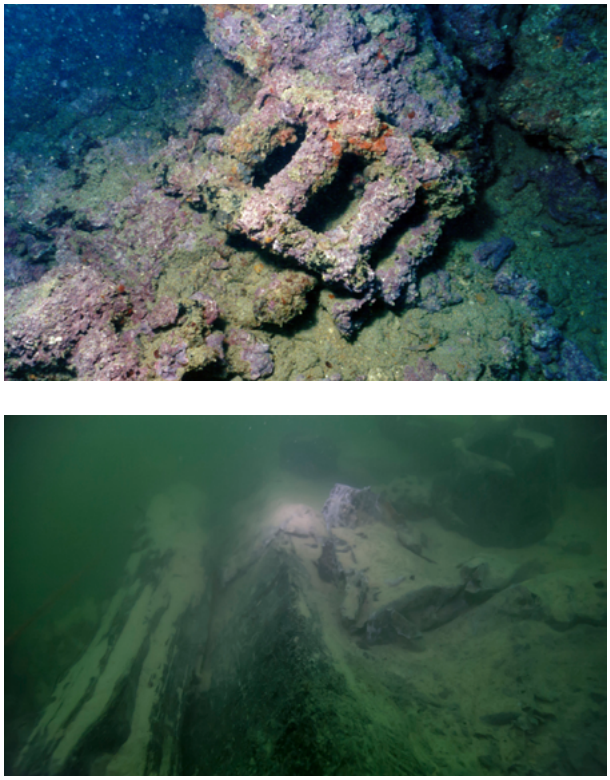


Image 13 |
On the left, LIBS spectra corresponding to sheathing from the *Bucentaure* (France), Mercante de San Sebastián (Spain) and the Delta II (Italy).

On the right and from the top down, a bilge pump wheel from the *Bucentaure*. Photo: IAPH Image Archives; lead sheathing from the shipwreck Delta II. Photo: Tanit Archaeological Management

order to correctly prevent water from entering the probe. The use of He or Ar considerably improves the LIBS signal.

The results obtained during the measurement campaigns organised at the archaeological sites of Chapitel and San Pedro de Alcántara were quite satisfactory and allowed, for the first time, for the examination and identification of underwater archaeological materials. Ceramic material, marble, bronze alloys, lead fragments and even iron cannons were detected and analysed. Moreover, the chemical composition of samples of sheathing from different shipwrecks was also correlated with the origins of these vessels.

Acknowledgments
This research was funded by the project P11-FQM-7193 (AQUALAS), a joint effort of Instituto Andaluz del Patrimonio Histórico (IAPH)/Centro de Arqueología Subacuática (CAS) and the University of Malaga (UMA). M. Lopez-Claros would like to acknowledge the Consejería de Innovación, Ciencia y Empleo of the Junta de Andalucía for her fellowship.

BIBLIOGRAPHY

BETHENCOURT, M.; BOCALANDRO, A.; ROMERO, J. (2011)
Datación de pecios de los siglos XVIII y XIX a través de la caracterización de los forros de cobre. En *IV Congreso Latinoamericano de Conservación y Restauración de Metal, Madrid (13 al 17 de septiembre de 2011)*. Madrid: Secretaría General Técnica, Ministerio de Educación, Cultura y Deporte; Grupo Español de Conservación, 2011, pp. 51-62

BONIFACIO, C. (2008)
Galeones con Tesoros. Dónde están hundidos, Qué llevaban. Brenes (Sevilla): Muñoz Moya Editores Extremeños, 2008

BOWEN, A. (2009)
Underwater Archaeology: The NAS Guide to Principles and Practice. 2nd ed. Portsmounth: Blackwell Publishing, 2009

CHARFI, B.; HARITH, M. A. (2002)
Panoramic laser-induced breakdown spectrometry of water. *Spectrochim. Acta Part B*, vol. 57, 2002, pp. 1141-1153

***CONVENTION** on the Protection of the Underwater Cultural Heritage* (2001). Paris: Unesco, 2001

CREMERS, D. A.; RADZIEMSKI, L. J.; LOREE T. R. (1984)
Spectrochemical analysis of liquids using the laser spark. *Appl. Spectrosc*., vol. 38, 1984, pp. 721-726

DE GIACOMO, A.; DELL'AGLIO, M.; COLAO, F. et al. (2004)
Double pulse laser produced plasma on metallic target in seawater: basic aspects and analytical approach. *Spectrochim. Acta Part B*, vol. 59, 2004, pp. 1431-1438

DE GIACOMO, A.; DELL'AGLIO, M.; DE PASCALE, O. et al. (2007)
From single pulse to double pulse ns-laser induced breakdown spectroscopy under water: elemental analysis of aqueous solutions and submerged solid samples. *Spectrochim. Acta Part B*, vol. 62, 2007, pp. 721-738

FANTONI, R.; BARBINI, R.; COLAO, F. et al. (2004)
Integration of two lidar fluorosensor payloads in submarine ROV and flying UAV platforms. *EARSeL eProc.*, vol. 3, 2004, pp. 43-53

FORTES, F. J.; CORTÉS, M.; SIMÓN, M. D. et al. (2005)
Chronocultural sorting of archaeological bronze objects using laser-induced breakdown spectrometry. A*nal. Chim. Acta*, vol. 554, 2005, pp. 136-143

FORTES, F. J.; CUÑAT, J.; CABALÍN, L. M. et al. (2007)
In situ analytical assessment and chemical imaging of historical buildings using a man-portable laser system. *Appl. Spectrosc.*, vol. 61, 2007, pp. 558-564

FORTES, F. J.; LASERNA, J. J. (2010)
The development of fieldable laser-induced breakdown spectrometer: no limits on the horizon. *Spectrochim. Acta Part B*, vol. 65, 2010, pp. 975-990

FORTES, F. J.; MOROS, J.; LUCENA, P. et al. (2013)
Laser-induced breakdown spectroscopy. *Anal. Chem.*, vol. 85, 2013, pp. 640-669

GIAKOUMAKI, A.; MELESSANAKI, K.; ANGLOS, D. (2007)
Laser-induced breakdown spectroscopy (LIBS) in archaeological science-applications and prospects. *Anal. Bioanal. Chem.,* vol. 387, 2007, pp. 749-760

GUIRADO, S.; FORTES, F. J.; CABALIN, L. M. et al. (2014)
Effect of Pulse Duration in Multi-Pulse Excitation of Silicon in Laser-Induced Breakdown Spectroscopy (LIBS). *Appl. Spectrosc*., 2014, vol. 68, pp. 1060-1066

GUIRADO, S.; FORTES, F. J.; LASERNA, J. J. (2015)
Elemental analysis of materials in an underwater archeological shipwreck using a novel remote laser-induced breakdown spectroscopy system. *Talanta*, vol. 137, 2015, pp. 182-188

GUIRADO, S.; FORTES, F. J.; LAZIC, V. et al. (2012)
Chemical analysis of archeological materials in submarine environments using laser-induced breakdown spectroscopy. On-site trials in the Mediterranean Sea. *Spectrochim. Acta, Part B*, vol. 74-75, 2012, pp. 137-143

LAZIC, V.; COLAO, F.; FANTONI, R. et al. (2005)
Recognition of archaeological materials underwater by laser induced breakdown spectroscopy. *Spectrochim. Acta Part B*, vol. 60, 2005, pp. 1014-1024

LAZIC, V.; LASERNA, J. J.; JOVICEVIC, S. (2013a)
Insights in the laser-induced breakdown spectroscopy signal generation underwater using dual pulse excitation. Part I: Vapor bubble, shockwaves and plasma. *Spectrochim. Acta, Part B*, vol. 82, 2013, pp. 42-49

LAZIC, V.; LASERNA, J. J.; JOVICEVIC, S. (2013b)
Insights in the laser-induced breakdown spectroscopy signal generation underwater using dual pulse excitation. Part II: Plasma emission intensity as a function of interpulse delay. *Spectrochim. Acta, Part B*, vol. 82, 2013, pp. 50-59

LEÓN AMORES, C. (2009)
Buceando en el Pasado. Madrid: Espasa Calpe, 2009

MARGETIC, V.; PAKULEV, A.; STOCKHAUS, A. et al. (2000)
A comparison of nanosecond and femtosecond laser induced plasma spectroscopy of brass samples. *Spectrochim. Acta Part B*, vol. 55, 2000, pp. 1771-1785

WHITE, S. N.; DUNK, R. M.; PELTZER, J. J. et al. (2006)
In situ Raman analyses of deep-sea hydrothermal and cold seep systems (Gorda Ridge and Hydrate Ridge). *Geochem, Geophys. Geosyst*, vol. 7, 2006, Q05023