Journal of Cultural Heritage xxx (2017) xxx–xxx

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Original article

Subsea spectral identification of shipwreck objects using laser-induced breakdown spectroscopy and linear discriminant analysis

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ARTICLE INFO

Article history:
Received 7 September 2016
Accepted 20 December 2016
Available online xxx

Keywords:
Laser-induced breakdown spectroscopy
LIBS
Underwater analysis
Multi-pulse excitation
Optical fiber
Cultural heritage

ABSTRACT

Underwater LIBS is an evolving technology which offers unique advantages over traditional methods, not only do it offers the composition of liquids with high reliability; it also provides the elemental composition of solids with little or no user manipulation. Because of this advantage, LIBS has been used as a tool for inspecting materials in underwater archaeology, where knowledge of the chemical composition may provide valuable clues on the origin of materials in shipwrecks and submerged buildings. This study attempts to provide undersea LIBS instrumentation with the data processing tools intended to make shipwreck inspection surveys easier and faster. The new tool has been designed to sort the readings obtained by a LIBS system when inspecting unknown pieces found in the sea bottom and assign their composition to one of several groups of common materials found in shipwrecks. The tool involves linear discriminant analysis that was first validated in the laboratory with a training set of samples collected from wreckages. Then, the method was used in an underwater survey in the Mediterranean Sea to sort the materials found in a shipwreck. In combination with high-definition video recording, this approach can provide an understanding of the materials and a permanent record of the unknown assets, this eliminating the need for underwater archaeologists to make handwritten notes of individual pieces while surveying shipwrecks.

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1. Introduction

Underwater cultural heritage is a rich source of information and a window to the past. In fact, the presence of specific elements (either greater or lesser percentage) in an archaeological material, namely chemical fingerprints, is of great interest for a better understanding of its age, provenance and manufacturing technology. Discovery of amphoras, cannons and metallic artefacts in their archaeological context could provide further information concerning the age and nationality of a shipwreck [1]. However, the severe conditions of the marine environment change the appearance of the underwater sites and distorts the idyllic image of the shipwreck until blending with the surroundings. Hence, artefacts and structures may be uncovered beneath sediments, chemically altered or even destroyed.

Recent advances in electronic engineering, underwater robotics and novel systems for processing and image recognition make localization of underwater archaeological sites much easier than in past. However, underwater archaeology still requires the development of screening techniques for the in-situ recognition of findings. A restricted number of laser-based techniques (i.e. Raman, LIBS and LIF) have proven to be useful for this purpose [2–4]. Specifically, LIBS is really appreciated as is the unique that could provide atomic information from the spectral signature of underwater objects [5,6]. Additionally, LIBS combines valuable attributes (no sample preparation, minimally destructive, fast analytical response and possibility of remote sensing analysis), specially demanded in cultural heritage preservation and investigation [7,8]. It's worth mentioning that underwater LIBS analysis is not a trivial task and several research groups have proposed different alternatives for improving LIBS sensitivity inside liquids [9–11]. In this sense, the dual pulse excitations being the most common approach proposed in the literature [12–14]. However, problems related to the use of two laser sources, the precise alignment needed and synchronization in data acquisition are obstacles for its implementation in field analysis [15,16]. The instrumental development was further investigated until 2012 when Guirado et al. [17] published the first in-situ undersea LIBS analysis of solid materials, at a depth of 30 m,

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http://dx.doi.org/10.1016/j.culher.2016.12.015
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Please cite this article in press as: M. López-Claros, et al., Subsea spectral identification of shipwreck objects using laser-induced breakdown spectroscopy and linear discriminant analysis, Journal of Cultural Heritage (2017), http://dx.doi.org/10.1016/j.culher.2016.12.015

using a fiber-based LIBS system. Later, a new generation of LIBS instruments based on transmission of a collinear sequence of multi-pulses through the optical fiber cable was proposed by the same authors to improve the performance of the technology [18,19]. An archaeological shipwreck situated 17 m deep was inspected using this approach [20].

In subaquatic archaeology, quantitative information turns crucial for planning restoration/conservation activities and taking decisions about whether the object should be moved from the underwater site or not. Nevertheless, LIBS strongly depends on matrix effects, pulse to pulse fluctuations, plasma-solid interactions, among other factors. In this sense, a broad number of fundamental studies have been reported to overcome the so-called fractionation effect [21–24]. Certain procedures such as internal standardization, background normalization, calibration-free analysis and the use of a double-pulse configuration has been explored so far for quantitative analysis of submersed materials. Most recently, Guirado et al. [25] evaluated the use of multi-pulse (MP) excitation as an effective solution to mitigate the fractionation effects observed in LIBS analysis of copper-based alloys. MP-LIBS also prevents the effect of ambient pressure on LIBS signal, thus demonstrating the feasibility of LIBS for quantitative analysis of bronze materials in a real underwater site.

In such a scenario, development of spectral libraries and data processing algorithms also improve the capability of LIBS for field measurements. Hence, from an archaeological point of view, both qualitative and quantitative information extracts compositional evidence that together with the use of chemometric methods may identify specific materials which could be related to ancient manufacturing or production processes [26]. A number of statistical methods including linear and rank correlation, principal component analysis (PCA), partial least-squares discriminant analysis (PLS-DA) and soft independent modeling of class analogy (SIMCA), among others have proved to group and classify ancient artefacts in archaeometric analysis [27]. In this work, a classification method is evaluated for the identification of chemical fingerprints in shipwrecks. A variety of archaeological objects has been previously characterized in laboratory using essentially the same operational conditions than those found undersea in order to ensure the effectiveness of the method during the recognition process in the site. Moreover, a set of sheathings from different shipwrecks were analyzed with the objective to perform a chronocultural sorting of these structural pieces. Based on this procedure, findings from the shipwreck of *San Pedro de Alcántara* (Malaga, Spain) were directly classified into metallic alloys, ceramics, rocks or marbles.

2. Materials and methods

The remote LIBS instrument and its construction have been described in a recent paper [20] so only a brief description of the instrument is given here. The system consists of two well-defined parts: a hand-held probe and a main unit, interconnected by means of an umbilical cable. The main unit comprises the optical module for laser-fiber coupling, the data acquisition module and the laser power supply.

The optical module consists of a polymethyl methacrylate structure, specially adapted in order to prevent the deposition of particles from the marine environment at the tip of the optical fiber. The module contains the laser head (Q-switched Nd:YAG laser operating at 1064 nm, Brilliant) and all the optical arrangements for launching the laser radiation into the fiber-optic cable (mounted in a *xyz* stage) and collecting the plasma light for the transmission to a spectrograph. The laser beam is transmitted through a 55-m long fiber optic cable that travels inside an umbilical cord which connects the probe to the optical module. At the end of the fiber, the hand-held probe focuses the laser beam onto the sample surface by an appropriate optical configuration. With this configuration, the spot size was established at 450 μm in diameter.

The same optical fiber is used for light gathering purposes. The plasma light is collected and returned to the optical module, where it is conducted to the data-acquisition module using an optical system used to focus plasma light into the spectrometer fiber-optic cable (2 m length, 600 μm diameter, NA0.22). The data-acquisition module, consisting of the spectrometer, the video converter and the PC components, was installed in the main unit. A pulse/delay generator (which externally controls the system) was also configured within this module. The spectrometer is a crossed Czerny-Turner design with a holographic diffraction grating of 1200 lines mm^{-1} (Avantes, model AvaSpec-2048-USB2). This configuration provides a spectral resolution of 0.1–0.2 nm/pixel in the spectral range of 300–550 nm. AvaSoft software was employed for controlling the spectrometer and for data processing. The acquisition delay was established in 1 μs which corresponds to the best signal-to-noise ratio (SNR) for the LIBS signal. The irradiance value at sample surface was 1.6 GW cm^{-2}. And all underwater analysis was carried out using 5 bars of argon as a purge gas. The Statgraphics® statistics software package was used for chemometrics analysis.

3. Results and discussion

3.1. Classification method for archaeological artefacts

Given the great compositional diversity, textural differences and surface alteration of the submersed cultural heritage, the use of advanced statistical algorithms is essential for the recognition and sorting of underwater findings. For this purpose, linear discriminant analysis (LDA) was used to generate a classification model from which unknown samples will be predicted in site on the basis of their LIBS response. As a supervised algorithm, a LDA model based on the spectra acquired from a set of known archaeological samples was constructed. LDA evaluates the relative weights of the original variables for group discrimination and score the separation between multiple classes [28–30]. Afterwards, the model predicts the probability that an unknown sample belongs to each class.

A set of 38 objects collected from several archaeological shipwrecks was first studied. To simulate the experimental conditions of a subsea environment, samples were immersed and analyzed in a water tank in our laboratory. Because of the large variety of samples used in this study, objects were divided into different groups for chemometric analysis, i.e. bronze-alloys (10 samples), metallic pieces (18 samples), ceramics (5 samples) and marbles (5 samples). LIBS spectra were acquired in the 350–550 nm spectral range and their intensities normalized to unity for comparative purposes. Data were acquired by averaging the response of 50 laser shots on three adjacent positions for each sample. However, the whole LIBS spectra were not considered as input data. From the initial information of 2048 data points, only 10 spectral variables were considered for analysis. The selected variables were Cu (I) 510.55 nm, Zn (I) 481.05 nm, Sn (I) 452.47 nm, Pb (I) 405.78 nm, Fe (I) 438.35 nm, Ca (I) 422.67 nm, Mg (I) 517.26 nm, Si (I) 390.55 nm, Sr (I) 407.61 nm and Ti (I) 498.17 nm. In addition, the presence of Ca, Mg, Si and Ti in metallic samples is associated to the deposition of sedimentary material on the sample surface. The first discriminant function has the expression:

$$F1 = 2.7 \cdot I_{Cu} + 2.4 \cdot I_{Zn} + 22.8 \cdot I_{Sn} + 0.8 \cdot I_{Pb} + 2.7 \cdot I_{Fe} - 7.2 \cdot I_{Ca} - 1.2 \cdot I_{Mg} - 3.8 \cdot I_{Sr} - 6.0 \cdot I_{Si+Ti} + 0.59$$

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