Recognition of archeological materials underwater by laser induced breakdown spectroscopy[☆]

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Abstract

The detection of different materials immersed in seawater has been studied by means of Laser Induced Breakdown Spectroscopy. The plasma emission was produced by a Q-Switched Nd:YAG laser operated at 1064 nm in a dual pulse mode. Different classes of materials potentially found in the undersea archaeological parks, such as iron, copper-based alloys, precious alloys, marble and wood have been examined. Data acquisition and processing were optimized for better signal control and in order to improve the detection threshold. In all the examined cases but wood, qualitative analysis was successful and allowed for the material recognition. The spectral features necessary to clearly distinguish marble materials from calcareous rocks have been also established. It was found that these characteristic spectral intervals could be also used for the recognition of sedimentary layers deposited on the underwater findings. Quantitative chemical analysis was also performed on submerged bronze samples, after generating calibration curves with standards of similar matrix composition.
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1. Introduction

Since prehistoric times, the Mediterranean Sea coasts were densely populated, hosting numerous harbors and ports. In this area, ship traffic was intense from ancient times up to the modern age. Due to storms, accidents and naval battles, the Mediterranean Sea-bottom is rich in archaeological findings relevant to wrecked ships. To the richness of the underwater patrimony, submersed coastal small settlements and towns also contribute. Nowadays, modern acoustic instruments (e.g. scanning SONAR) are available and localization of the underwater relicts and ruins has become much easier than in the past. Nevertheless, the problem of recuperating only the most valuable findings and

their discrimination from useless ballasts still remains and its solution necessitates the development of fast, in-situ screening techniques. An additional request for underwater recognition of the archaeological findings currently comes from the institution of numerous marine parks, where the submerged sites may be visited, either virtually or by diving. Also in this case, the objects present in the site must be catalogued and possibly restored underwater, especially when highly oxidized surfaces are encountered. Once again, analytical in situ techniques must be used to characterize the surfaces, preferentially during the cleaning action [1,2].

The advantages of Laser Induced Breakdown Spectroscopy (LIBS) [3–5] over other quantitative techniques for elemental analyses applicable on historical findings are mainly its low invasiveness, the possibility to perform in-situ measurements, and its high spatial discrimination and rapidity of analysis [6]. Development of new spectrometers with a sufficiently high spectral resolution, such as Echelle [7,8], and fiber based modular units [9] allows for simultaneous detection over wide spectral ranges, thus enlarging the number of elements that can be detected. LIBS has been

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successfully applied to characterize different artwork surfaces in air, including marbles [10,11], pigments [6,12,13], multi-layered ceramics [14,15] and metals [14]. The analytical capabilities of the technique when applied to underwater samples were significantly increased by the implementation of double pulse laser excitation [16–19]. Here, the first laser pulse produces a cavitation bubble [20] while the second probing pulse further ablates the sample and excites the plasma inside the bubble. In this way, an intense and narrow spectral emission might be observed, the latter feature being due to the relatively low pressure environment inside the bubble. Underwater detection of submersed metallic samples by dual-pulse LIBS has been recently demonstrated [19,21]. An alternative approach for a direct underwater recognition of some materials by LIBS has been proposed by Beddows et al. [22], where a gas flux was applied to create sample-air interface prior to the laser ablation. However, the described LIBS system is rather complex and can not be used for bulk water analysis.

An Italian research project, named TECSIS (diagnostics and technologies and intelligent systems for a development of archaeological parks in Southern Italy) deals explicitly with development of innovative techniques suitable for submarine archaeology. In the framework of this project, we have carried out laboratory experiments on various types of materials, characterized by different levels of surface preservation, which were immersed in artificial seawater. Different metals have been examined, since their qualitative analysis is of great importance to support the decision of recuperating the finding, namely the recognition of precious metals (gold, silver and their alloys) and to discriminate bronze artefacts from iron masses used for ballasts, working tools or ship construction. Quantitative underwater analysis of bronze samples have been also performed, in view of the possibility of dating the objects, as the lead content varied along the ancient age [23]. Stone materials have also been considered, in particular the discrimination of marble from common calcareous stones, given the widespread use of marble both for architectonic elements and decorative objects in the classical period. Underwater recognition of wood has been also examined, also considering that this type of material requires a special recovery procedure under controlled atmosphere in order to prevent fast destruction of the sample after its transfer in the air surrounding.

The aim of this work is to illustrate the results obtained on different kind of samples, together with a discussion of the experimental laboratory set-up and the data analysis procedures, optimized for the measurements on submersed samples. The optimization of the technique has been performed both through the choice of experimental parameters and by an appropriate signal post-processing filtering technique, described in detail in another paper [25]. The results will also be discussed in view of the specific problems relevant to submarine archaeology.

2. Experimental

2.1. Laboratory set-up

The plasma emission was produced by a Q-Switched (QS) Nd:YAG laser (Quanta System, model Handy Nd:YAG) operated at 1064 nm, with a repetition rate of 10 Hz and in a dual pulse mode. The laser QS trigger has been externally controlled in order to extract two laser pulses during the same lamp flashing, each one with duration of about 8 ns [24]. The laser pulse energies were varied by changing the time delay between the lamp trigger and the two QS triggers: $t_1 = 145 \div 155$ μs, $t_2 = 55 \div 75$ μs. The maximum laser energy, summed over the two pulses, was 320 mJ. Temporal separations between the triggers (and corresponding laser energies) were optimized for the best optical signal characteristics on a given type of submerged target (Table 1). For a fixed pulse separation, the energy of both pulses could be changed simultaneously by regulating the current through the laser flashlamps. At a fixed pumping level, the energy partition between two pulses mainly depends on the first trigger delay—for shorter delays the energy of the first pulse is lower, as illustrated in our companion work [25]. The laser beam was focused on the sample surface with two plano-convex lenses ($f_1 = 150$ mm, $f_2 = 25$ mm in the air), where the second lens was directly mounted on a beaker wall, so its surface was in contact with the water. The resulting back focal length in water was about 40 mm. The use of two lenses allowed for tighter focusing, which is required in the case of bulk water analyses in-situ by the same system [25]. The light emitted by the plasma in the UV–visible region

Table 1
Optimized experimental conditions for different materials

Material	Trigger delays (μs)	Pulse energies (mJ)	Laser shots	Acquisition gate (ns)	Acquisition delay (ns)
Stainless steel			20		
Iron—clean			20		
Bronze	$t_1 = 150$, $t_2 = 55$	$E_1 = 120$, $E_2 = 160$	20	400	100
Corroded iron			100		
Precious alloys			1		
Marble, rock	$t_1 = 145$, $t_2 = 55$	$E_1 = 82$, $E_2 = 180$	50	600	200
Wood in air[a]	$t = 210$	$E = 300$	20	1000	500
Bronze—quantitative measurements		$E_1 = 52$, $E_2 = 140$	20	1000	800

[a] Single pulse excitation.