



Review

Laser Induced Breakdown Spectroscopy in archeometry: A review of its application and future perspectives[☆]

Valeria Spizzichino^{*}, Roberta Fantoni

ENEA (Italian national agency for new technologies, energy and sustainable economic development), Technical Unit for the Development of Applications of Radiations, Via E. Fermi, 45, 00044 Frascati, Rome, Italy

ARTICLE INFO

Article history:

Received 28 February 2014

Accepted 14 July 2014

Available online 22 July 2014

Keywords:

LIBS

Archeometry

LIF

Raman

Indirect dating

ABSTRACT

Laser Induced Breakdown Spectroscopy (LIBS) in the last decades has been more and more applied to the field of Cultural Heritage with great results obtained either alone or in combination with complementary laser techniques. Its ability to analyze, with a minimal loss, different kinds of materials in laboratory, in situ and even in hostile environments has been highly appreciated. The main aim of this paper is to present a review of LIBS applications in the interdisciplinary field of archeometry. The LIBS technique is shortly described both from a theoretical and practical point of view, discussing the instrumental setup, also in comparison with typical features of laser induced fluorescence (LIF) and Raman spectroscopy apparatus. The complementary with multivariate analysis, a method that can help in reducing data set dimensions and in pulling out effective information, is stressed. In particular the role of LIBS in Cultural Heritage material characterization, recognition of fakes and indirect dating is described, reporting general considerations and case studies on metal alloys, mural paintings, decorated ceramics, glasses, stones and gems.

© 2014 Elsevier B.V. All rights reserved.

Contents

1. Introduction	201
2. The LIBS technique	202
2.1. LIBS principles	202
2.2. LIBS set-up: systems developed for CH surface characterization	202
2.3. LIBS combination with other techniques – respective principles	203
2.3.1. LIF	203
2.3.2. Raman	203
2.3.3. Multivariate analysis	204
3. Applications	204
3.1. Cultural Heritage material characterization	204
3.2. Recognition of fakes and restorations	205
3.3. Indirect dating	207
4. Conclusions	208
References	208

1. Introduction

At the very beginning archeometry was intended as the application of novel physical technologies to the dating of archeological findings

that were difficult to date by archeologists' conventional methods like stratigraphy. Nowadays archeometry means, more in general, the application of modern experimental methods and techniques in dating, investigation and identification of materials constituting ancient artifacts and the consequences of such studies in the related fields of archeology and art history. Then, it is clear that archeometry is an interdisciplinary subject covering both scientific and humanistic fields, including in the former analytical chemistry and spectroscopy, organic and biological chemistry, electrochemistry, and physics and in the latter anthropology,

[☆] Selected paper from the 7th Euro-Mediterranean Symposium on Laser Induced Breakdown Spectroscopy (EMSLIBS 2013), Bari, Italy, 16–20 September 2013.

^{*} Corresponding author.

E-mail address: valeria.spizzichino@enea.it (V. Spizzichino).

history, history of art and archeology, conservation science, and museology. Working on vulnerable, fragile and rare artifacts that often have a social importance associated to their historical value is challenging. In particular it is necessary to develop more and more appropriate techniques, that alone or in combination, can provide as much as possible exhaustive information.

After x-ray studies, radiocarbon, amino-acid and thermo-luminescence dating, and land and submarine prospecting, which were the main scientific methodologies initially applied to the field, nowadays laser techniques are becoming more and more popular. In fact they offer both practical and analytical advantages. The formers include the possibility to work remotely (often with only the need of an optical access), without the use of ionizing radiations, with limited or no chemical pre-processing and with no or minimal invasiveness. The latter ones concern the ability to provide qualitative and quantitative information on atomic and molecular composition and on colors.

In particular, Laser Induced Breakdown Spectroscopy (LIBS) in the last decades has been more and more applied to the field of Cultural Heritage (CH) with great results obtained either alone or in combination with complementary laser techniques. Its ability to analyze materials with different properties (e.g. both conductors and insulators) in various environments, in laboratory or in situ conditions, including extreme conditions (such as space or submarine exploration), with a minimal loss of material, has been highly appreciated. Qualitative and quantitative data on elemental composition derived from LIBS can be integrated with results from complementary laser methods, as laser induced fluorescence (LIF) and laser Raman spectroscopy. LIBS can be applied to the characterization of materials used for small and large artworks, supporting studies of historians of art and suggesting suitable conservation actions. The type of information derived can also help in the individuation of late retouches and fakes.

An important LIBS application for CH is the indirect dating. In fact, archeological materials can be dated on compositional analysis, on the basis of the presence of specific elements related to a technologic development. This kind of procedure has been exploited especially for inorganic materials in the absence of biological residuals. In particular the presence of some constituent elements marks the progress of metallurgy (in metallic artifacts) or of chemistry (in other artifacts like paints, pottery, glass, textiles, paper and inks). Additionally the presence of trace elements may reveal the use of specific tools (as metal alloys for carving stones) or be associated to characteristic contaminants on surface layers prior to restoration. Provenance studies might also help dating, in relation with specific quarries or mines utilized since a known period or reachable only after proper development of traveling facilities and related trades.

In next sections a review on experimental apparatus of LIBS and complementary laser based techniques utilized, either separately or in combination, and on CH material characterization, recognition of fakes and indirect dating is presented together with some case studies.

2. The LIBS technique

2.1. LIBS principles

When a high power density laser beam is focused onto the surface of a solid or liquid or in a small volume of a gaseous sample, the temperature of the interested region increases quickly up to the vaporization threshold. If the power density of the laser is above a critical value (which depends on the nature of the material, but is usually approximately 10^9 W cm^{-2} [1]), a chain of ionization – the breakdown – that leads to the plasma formation, whose temperature may reach 10^5 K , initiates. The breakdown consists of several phenomena, such as emission of photoelectrons, thermal ions and neutral molecules in the plasma, and sample heating with phase change at the surface. Different processes occur in sequence during the evolution of the laser induced plasma: initially a continuous Bremsstrahlung emission takes place and

successively plasma expands and cools. During the latter plasma relaxation, line emissions between bound states become detectable. These lines are already present immediately after the plasma formation, but are embedded in the continuous emission. Therefore, total plasma radiation appears initially as a continuous spectrum and later is composed by lines from spontaneous decays of electronically excited fragments, i.e. atoms, ions and small molecules. The continuous signal lowers quickly as the plasma cools; on the contrary, peaks due to fragment emission last much longer. Once the delay time and the integration gate are chosen, the signal can be acquired. It is then possible to retrieve plasma characteristics from both the time-resolved and frequency-resolved analyses of the emitted radiation. This is possible during the first phase, as well as after the equilibrium is reached. So, calculating electron density and temperature, it is possible to define the conditions of the generated plasma in the time window examined. Nowadays it is well ascertained that the LIBS technique can supply directly quantitative information on the evaporated material only upon very specific conditions: both stoichiometric evaporation and local thermodynamic equilibrium (LTE) should occur, and moreover the plasma should be optically thin [2,3]. The amount of induced plasma, as well as its stability, temperature, electron density, composition and temporal evolution depend on many parameters, related both to the involved material (such as the reflectivity of the surface, its absorption coefficient, its thermo-dynamical properties) and to the laser characteristics.

The generation of a laser-induced plasma and the analysis of the emitted signal require a rather simple experimental set-up, although the understanding of phenomena occurring in this frame still needs a significant amount of experimental and theoretical work. For this reason, technological applications of LIBS have been accompanied by a parallel and equally fundamental investigation on the relevant plasma, in particular concerning its generation and evolution.

2.2. LIBS set-up: systems developed for CH surface characterization

The specific application to which an apparatus is devoted drives the characteristics of the single constituents, mainly laser wavelength and pulse duration for excitation, spectrometer and detector.

The most common configuration for a LIBS apparatus consists in a solid state pulsed laser focused by simple fused silica convergent lens on the target, an optical system for the collection of the emitted signal and a Czerny–Turner spectrometer coupled to a solid-state multichannel detector. Depending on materials' properties, usually, different harmonics of a Nd:YAG laser are used as light source; in fact the efficiency of a particular λ coupled to the specific sample can have several effects on the resulting LIBS emissions, related to the amount of material ablated, emission intensity, and reproducibility [2,4], and often the fundamental wavelength at 1064 nm is preferred, for the higher energy available and the lower complexity of the laser source with respect to the use of harmonics. Significant exceptions concern CH materials with high ablation threshold (e.g. ceramic and glasses), which might require photochemical processes at the surface induced by UV ablation. Note that, using the same laser energy, the plasma temperature reached after UV excitation is lower and fewer ions are present in the plume, which might give rise to a lower limit of detection in tracing most elements detected as atoms [5,6]. However, the latter point is a drawback in few cases in which the elements of interest have ionic lines easier detectable than the atomic ones (e.g. alkaline earth metals) [7].

Compact spectrometers can be generally employed in applications where there is not much overlapping of lines or the elements of interest have simple spectra. However, CH samples, including historical alloys, presenting multilayered surfaces due to the realization process (paints, ceramics), to additional surface treatment (gilding, protective layers, consolidants), and to environmental factors (pollution, biodegradation), are well far from these simple cases. Usually a high resolution spectrometer is required, with data acquisition in a large spectral range (Echelle spectrometers), to retrieve semi-quantitative data on the

Download English Version:

<https://daneshyari.com/en/article/7674663>

Download Persian Version:

<https://daneshyari.com/article/7674663>

[Daneshyari.com](https://daneshyari.com)