Spectrochimica Acta Part B 101 (2014) 288–311

Contents lists available at ScienceDirect

Spectrochimica Acta Part B

journal homepage: www.elsevier.com/locate/sab

Review

Laser induced breakdown spectroscopy inside liquids: Processes and analytical aspects

V. Lazic [a,*], S. Jovićević [b]

[a] ENEA (UTAPRAD-DIM), Via. E. Fermi 45, 00044 Frascati (RM), Italy
[b] Institute of Physics, University of Belgrade, 11080 Belgrade, Serbia

ARTICLE INFO

Article history:
Received 27 May 2014
Accepted 5 September 2014
Available online 16 September 2014

Keywords:
Laser induced plasma
Laser induced bubble
LIBS
Liquid
Ablation

ABSTRACT

This paper provides an overview of the laser induced breakdown spectroscopy (LIBS) inside liquids, applied for detection of the elements present in the media itself or in the submerged samples. The processes inherent to the laser induced plasma formation and evolution inside liquids are discussed, including shockwave generation, vapor cavitation, and ablation of solids. Types of the laser excitation considered here are single pulse, dual pulse and multi-pulse. The literature relative to the LIBS measurements and applications inside liquids is reviewed and the most relevant results are summarized. Finally, we discuss the analytical aspects and release some suggestions for improving the LIBS sensitivity and accuracy in liquid environment.

Contents

1. Introduction . . . 289
2. Fundamentals . . . 289
 2.1. Optical properties of water . . . 289
 2.2. Laser induced breakdown in liquids . . . 290
 2.3. Laser induced cavitation and shockwaves . . . 292
 2.4. Laser ablation in liquids . . . 293
 2.5. Single pulse versus dual or multi pulse laser excitation . . . 295
3. LIBS measurements inside liquids . . . 298
 3.1. Analysis of bulk liquids . . . 298
  3.1.1. Plasma stability and effects of analytes . . . 298
  3.1.2. Results of bulk-liquid analysis . . . 299
  3.1.3. Effects of liquid pressure . . . 300
  3.1.4. Matrix effect . . . 302
 3.2. Direct analysis of submerged solid targets . . . 302
  3.2.1. Single pulse LIBS on submerged solids . . . 302
  3.2.2. Dual pulse LIBS on submerged solids . . . 303
 3.3. Analysis of submerged targets under gas flow . . . 305
 3.4. Analysis of submerged soft materials . . . 306
 3.5. Analytical aspects . . . 306
4. Conclusions . . . 309
Acknowledgments . . . 309
References . . . 309

* Corresponding author.
E-mail address: violeta.lazic@enea.it (V. Lazic).

http://dx.doi.org/10.1016/j.sab.2014.09.006
0584-8547/

1. Introduction

Laser induced breakdown spectroscopy (LIBS) is based on plasma generation by short and intense laser pulses focused on solid, liquid or gaseous samples. The spectrally resolved detection of the plasma radiation, which contains the excited atoms and ions originating from the sample, provides qualitative and quantitative information about the elements present in the material. Although LIBS has not yet reached very high sensitivity and accuracy compared to some other laboratory methods, it has been tagged as a superstar analytical technique [1] due to its inherent advantages such as: i) measurement capability in any environment: inside gases and liquids of any type and pressure; ii) characterization of any type of the sample: solid, liquid, gaseous, and aerosols; iii) sample preparation is not necessary; iv) the measurements are in real-time and might be implemented in-situ; v) the probing is contactless and might be performed at distances also beyond 100 m; vi) the costs of the LIBS instruments are relatively low compared to other equipment with analogue performances; and vii) the instrument might be compacted to a portable format.

Due to an increased importance and wide-spread use of the LIBS technique, different review papers have been recently published, mainly focused on: history of LIBS and the instrument developments [2], a comprehensive overview of the processes involved in LIBS [3], instrumentation and methodology for material analysis [4], portable and stand-off LIBS instruments [5,6], detection and modeling of the plasma and its parameters [7,8], biological [9,10] and biomedical applications [11,12], soil analysis [13], and some specific applications such as environmental monitoring, space exploration and cultural heritage [14]. The developments in LIBS over the years 2008–2012 are reviewed by F.J. Fortes et al. [15].

Presently, LIBS is the only available technique for direct elemental analysis of bulk liquids and submerged targets. The chemical characterization of bulk liquids might be employed for in-situ detection of leakages in industrial and power plants [16–18], other kinds of water contamination [19,20], geothermal winds in deep oceans [21,22], and direct analysis of liquids inside transparent containers [23]. Characterization of the submerged materials could be exploited also for feedback control in laser surgery, usually performed with liquid coverage [24], then for recognition of underwater building materials and archeological objects [25,26], and determination of recent pollution or bio-activity in waters through sampling of seabed's surface [27].

The laser driven plasma formation and excitation on or inside liquids are not efficient processes because a great portion of the laser energy is expended for liquid vaporization. Both water and organic solutions contain hydrogen, which contributes to a rapid thermalization and cooling of the plasma. In water, due to abundance of oxygen atoms, different plasma species undergo rapid oxidation; this reduces availability of the excited analyte atoms or ions. Once the plasma is created inside liquid, the high density and nearly incompressible medium strongly confines the plume; the corresponding effects on the plasma evolution and LIBS signal are discussed in [28]. Plasma formation inside liquids is accompanied by emission of intense shockwaves, which affect the ablation threshold and rate of submerged targets. The plasma emission and expansion are followed by growth of a vapor cavity, which lifetime can exceed a few milliseconds.

Although the LIBS applications inside liquids raised a large interest for in-situ measurements and a number of works reported the relative studies, the last review paper about underwater LIBS, by De Giacomo and co-workers, was published in 2007 [29]. Some discussion about LIBS in liquids is also given in one section of [28] — the review paper about the effects of the background environment on the plasma formation, evolution and its optical emission. The LIBS technique applied on or inside liquids is concisely discussed by Lazic in the book chapter 6 of [30], where following cases were considered: ablation of a free surface (static, flowing and jet), breakdown on droplets and liquid aerosols, ablation of frozen solutions, breakdown in the media and sample ablation inside liquids.

In the present paper we focus on LIBS measurements inside bulk liquids, relative both to the solutes and to the submerged solid samples. The relevant processes involved in plasma formation and evolution are described, and the results obtained by various research groups are discussed. Finally, we present different analytical aspects to take into account when performing the measurements and the data processing.

2. Fundamentals

2.1. Optical properties of water

The most common liquid involved in the LIBS experiments is water, and in this section we discuss briefly its optical properties, relevant for the plasma formation and detection.

A complex index of refraction $\tilde{n} = n + ik$ contains the real part n that indicates the phase velocity, while the imaginary part k is related to the absorption losses when the electromagnetic wave propagates through the material. The real part n of the refractive index of water smoothly decreases with the wavelength in the range 200–1200 nm (Fig. 1 — top), which is of interest for LIBS [31]. Refractive index of pure water at room temperature and atmospheric pressure is between 1.394 and 1.326 in the range of 226–1013 nm [32]. The imaginary part k of the complex refraction index of water is also tabulated for

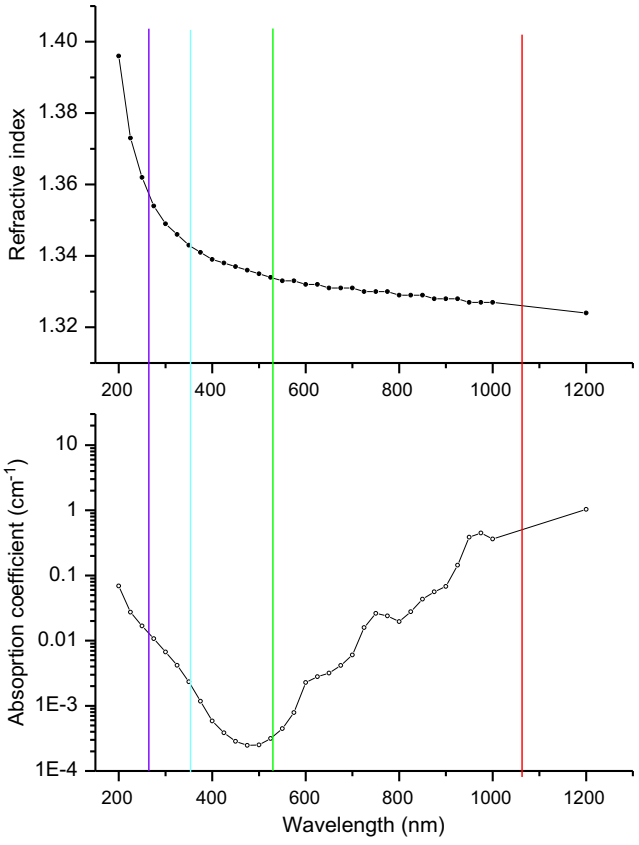

Fig. 1. Refractive index (top) and absorption coefficient (bottom) of pure water at room temperature and pressure as a function of wavelength — data from [31]; the vertical lines indicate the wavelengths of Nd:YAG laser: 1064 nm (red), 532 nm (green), 355 nm (light blue) and 266 nm (violet). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)