

Characterization of materials by means of laser-based techniques

L. Caneve

ENEA, CR Frascati, Rome, Italy

E-mail: luisa.caneve@enea.it

Abstract. Laser-based techniques are more and more used in the field of materials processing and analysis. In particular, laser spectroscopic techniques as the Laser Induced Breakdown Spectroscopy (LIBS) and Laser Induced Fluorescence (LIF) have been applied to investigate the chemical-physical properties and the morphological structure of several kinds of materials. Some results in different fields of application are reported.

1. Introduction

The application of laser-based techniques as analytical tools in materials science is widespread and very promising by now, also due to the continuous development of the laser technology. In this work, in particular, the attention will be focused on two spectroscopic laser techniques: Laser Induced Breakdown Spectroscopy (LIBS) and Laser Induced Fluorescence (LIF).

Laser induced breakdown spectroscopy (LIBS) is an atomic emission spectroscopic technique. It is based on the spectral analysis of the radiation emitted by a plasma generated by the interaction of an intense laser radiation with a material sample. The elemental composition of the investigated sample can be determined from the analysis of the emission spectrum [1] and the element concentrations theoretically deduced [2]. LIBS is particularly suitable for rapid on-line analysis. Nowadays, LIBS has reached a mature stage for analytical applications on a wide range of materials in solid, liquid and gas phase [3]. Good results have been obtained by LIBS on surface and sublayers analysis.

The emission of radiation by luminescent materials is observed whenever an absorption of energy sufficient to activate allowed electronic transitions occurs. Laser induced fluorescence (LIF) is a molecular spectroscopy based on the interaction of the ultraviolet radiation emitted by a laser with the matter [4]. This technique, for a surface analysis, is fast, remote, non invasive and specific. Through the study of the fluorescence emission spectrum is possible to obtain information of analytical and qualitative interest [5]. Both techniques have been used in many fields of application.

2. Experimental

In the laboratory of laser applications of ENEA Frascati, LIBS and LIF experimental equipments have been developed.

2.1 LIBS apparatus

The LIBS apparatus has fully described in its general configuration elsewhere [6], here the main characteristics will be recalled. In 'Fig.1' a scheme is reported. The radiation source is a Nd:YAG laser (Handy Quanta System) working usually at the fundamental wavelength of 1064 nm and focalized by a lens on the surface of the studied sample. The plasma emissions were collected by suitable receiver optics and the optical signal was carried by an optical fiber to the entrance slit of monochromator (Jobin Yvon model TRIAX550) equipped with three different gratings.

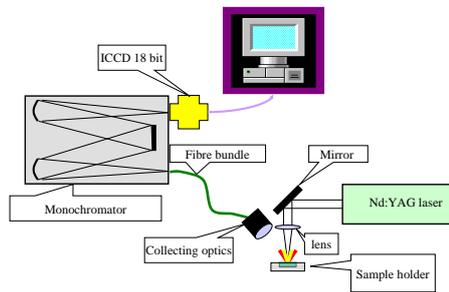


Fig. 1- Scheme of LIBS apparatus

The LIBS spectra were detected and recorded by a multichannel analyzer based on a gated ICCD, model Insta Spec IV. The experimental and acquisition parameters (energy laser, laser shots number, acquisition delay from the laser pulse, acquisition temporal gate) depend on the specific application. Stratigraphic analysis [7] with the identification of the chemical elements present at different depth is possible recording the LIBS spectra from the same point of the sample at increasing laser shots number.

Some advantages offered by LIBS make it very useful in many different applications: no sample pre-treatment is required, measurements can be performed directly in situ, in hostile environment too, on line data analysis is possible. Furthermore, LIBS is a fast spectroscopic method.

2.2 LIF apparatus

An innovative compact scanning LIF system has been developed at the ENEA of Frascati, based on a previous instrument's version [8]. The layout of the system is given in 'fig. 2'. The radiation source is a Thomson DIVA diode pulsed Nd:YAG laser, able to produce laser pulses both at 266 and 355 nm with a time duration of 10 ns at a fluence from 1 to 50mJ/cm². The main advantages of this new version are its reduced size, all the mechanical and optical elements have been installed in an aluminum box of 58×43×36 cm³ for less than 15kg, its small size and light weight that allow for an easy transfer of the system, and its operation from scaffoldings, in case of surfaces out of the current maximum range for remote operation (10 m). The spectrometer entrance is protected from the intense backscattered radiation by means of an appropriate dichroic filter. The digitized spectrum is transferred to a portable computer where a LabView program allows the user to set experimental parameters, to control data acquisition, and to perform a preliminary data analysis.

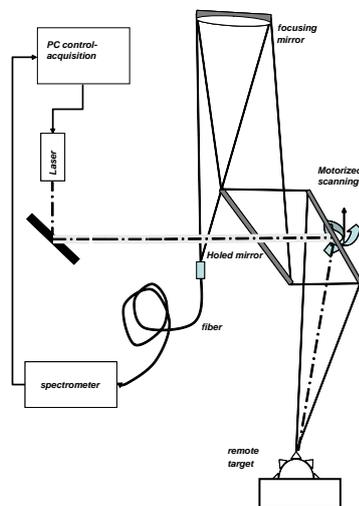


Fig. 2 – Scheme of LIF apparatus

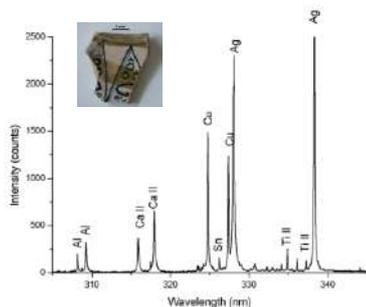


Fig. 3 - LIBS spectrum of ancient ceramic

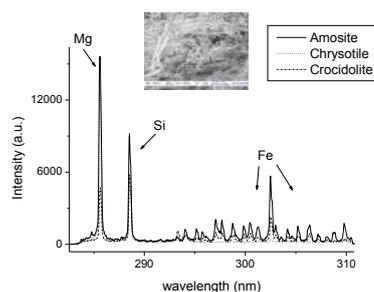


Fig. 4 - LIBS spectra of asbestos

The main advantages offered by this technique are the possibility to perform measurements in real time, in-situ without sample preparation, besides its minimum invasiveness.

3. Applications

Laser Induced Breakdown Spectroscopy and Laser Induced Fluorescence present several advantages with respect to other spectroscopic techniques and can be utilized for a variety of prompt analytical applications on different materials. Some applications will be reported on the following.

3.1 LIBS applications

LIBS has found in the Cultural Heritage preservation a fertile field of application due to its minimally invasive and only micro-destructive feature, the availability of portable instruments and the possibility of stratigraphy with on-line monitoring cleaning processes. These characteristics makes the technique suitable for qualitative and quantitative multi-elemental analyses on a large variety of samples surfaces in most different stages of preservation. Analysis of pigments [9] and different kinds of ancient materials as copper based alloys [10], ceramics [11,12] and marbles [13], for examples, has been performed by LIBS.

In ‘Fig.3’ a typical spectrum of gold lustre with silver and copper lines, emission line from Sn is coming from the underlying glaze, from a decorated Renaissance umbrian ceramic is shown.

LIBS has been successfully applied in laboratory analyses of soils and sediments, in order to trace the presence of heavy metals as pollutants [14] or to investigate sedimentation processes in natural ecosystems (Ross Sea, Antarctica) [15]. Among the environmental applications, the possibility of detecting and identifying asbestos by LIBS technique (‘Fig.4’) in samples of different kind, as for example building materials, has been demonstrated [16].

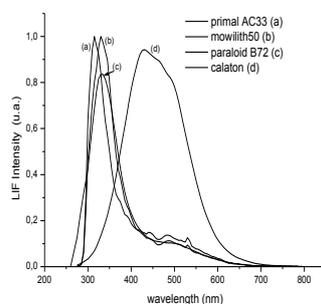


Fig. 5 - Fluorescence spectra at $\lambda_{exc}=266nm$ of acrylic resins

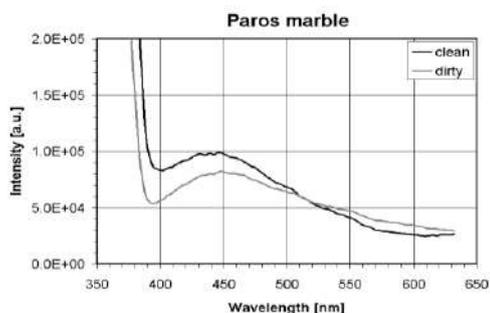


Fig. 6 – LIF spectra at $\lambda_{exc} = 355$ nm of Paros marbles clean and with crust

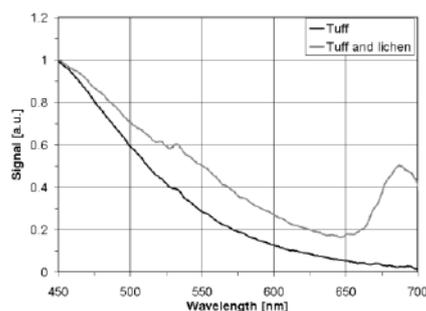


Fig. 7 – LIF spectra at $\lambda_{exc} = 355$ nm of tuff and deteriorated tuff.

The LIBS applicability in situ makes it one of the most interesting techniques to carry out remote measurements inside a tokamak vacuum chamber directly, without any removal of the internal coverings.

A recent study aimed to assess the diagnostic potentialities of the LIBS technique for the qualitative and quantitative determination of superficial contaminants deposited and/or adsorbed on the superficial coating of a tokamak reactor, has been led [17].

3.2 LIF applications

The performance of laser induced fluorescence (LIF) as a diagnostic tool for cultural heritage has been evaluated by exploiting the ENEA scanning LIF system to investigate different materials relevant in this field of application. The possibility to detect and discriminate different acrylic resins on fresco has been demonstrated both on laboratory samples and on original wall paintings by in situ measurements [18,19]. In 'Fig.5' the fluorescence spectra corresponding to four different resins are reported.

The effect of deteriorating agents on different materials has been investigated. The presence of a detrimental crust on a marble from Paros due to the external exposure has been well emphasized by the LIF signal, as can be seen in 'Fig.6'.

The detrimental effects on tuff surfaces of biodegrading agents, as fungi and lichens, has been detected by LIF allowing to observe characteristics invisible with the naked eye while avoiding to move sample from their original location. In 'Fig.7' the chlorophyll fluorescence emission at 680 nm from a deteriorated area respect to a clean one reveals the presence of a biodegradation process.

In conclusion, laser-based techniques can be used in the field of materials analysis with good results and many fields of application are possible. The experimental conditions need to be optimized according to the specific application.

Acknowledgments

All activities reported in this paper have been developed with my colleagues: F. Colao, R. Fantoni, L. Fiorani, V. Lazic, A. Palucci.

4. References

- [1] R. Wisbrun, I Schechter, R. Niessner, H. Schroeder: *SPIE* **1716** 2-14 (1992)
- [2] E. Tognoni, V. Palleschi, M. Corsi, G. Cristoforetti: *Spectrochimica Acta B* **57** 1115-1130 (2002)
- [3] J.D. Winefordner, I.B. Gornushkin, T. Correll, E. Gibb, B.W. Smith, N. Omenetto: *J. Anal. At. Spectrom.* **19** 1061-1063 (2004).
- [4] J. L. Kinsey: *Ann. Rev. Phys. Chem.* **28** 349-372 (1977)
- [5] D. Lognoli, G. Lamenti, L. Pantani, D. Tirelli, P. Tiano, L. Tomaselli: *Appl. Opt.* **41** 1780-1787 (2002)

- [6] F. Colao, R. Fantoni, V. Lazic, L. Caneve, A. Giardini, V. Spizzichino . *J. Anal. At. Spectrom.*, **19** 502-504 (2004).
- [7] D. Anglos, S. Couris, C. Fotakis: *Appl. Spectrosc.* **52** 1025-1030 (1997).
- [8] F. Colao, L. Caneve, R. Fantoni, L. Fiorani, A. Palucci: “Lasers in the Conservation of Artworks” *Proceedings of LACONA 2007, Madrid, 2007*, Marta Castillejo, Pablo Moreno, Mohamed Oujja, Roxana Radvan, Javier Ruiz Eds. (CRC Press).
- [9] M. Castillejo, M. Martin, D. Silva, T. Stratoudaki, D. Anglos, L. Burgio, R.J. Clark: *J. Mol. Struct.*, **550–551** 191–198 (2000).
- [10] L. Caneve, F. Colao, R. Fantoni, V. Spizzichino: *Appl. Phys. A*, **85** 151-157 (2006).
- [11] J.M. Anzano, M.A. Villoria, I.B. Gomushkin, B.W. Smith, J.D. Winefordner: *Can. J. An. Sc. Spec.* **47** 134-140 (2002).
- [12] V. Lazic, F. Colao, R. Fantoni, A. Palucci, V. Spizzichino, I. Borgia, B. Brunetti, A. Sgamellotti: *J. Cultural Heritage* **4** 303s-308s (2003).
- [13] P. Maravelaki-Kalaitzaki, D. Anglos, V. Kilikoglou, V. Zafirooulos: *Spectrochimica Acta B* **56** 887-903 (2001).
- [14] Capitelli, F., Colao, F., Provenzano, M.R., Fantoni, R., Brunetti, G., Senesi N.: *Goederma*, **106** 46 – 62. (2002)
- [15] Barbini, R., Colao, F., Lazic, V., Fantoni, R., Palucci, A., Angelone M.: *Spectrochimica Acta B* **57** 1203-1218 (2002).
- [16] L.Caneve, F.Colao, R.Fantoni, V.Spizzichino: *Spectrochimica Acta B* **60** 1115-1120 (2005).
- [17] L.Caneve, F.Colao, R.Fantoni: *ENEA RT/2008/52/FIM*
- [18] L.Caneve, F. Colao, R. Fantoni, L. Fiorani, L. Fornarini: *Proceedings of the 2nd OSAV International Conference, Saint Petersburg, 2008*, 57-63.
- [19] F. Colao, R. Fantoni, L. Fiorani, A. Palucci *ENEA RT/2006/FIM*