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Remote characterization of multilayered surfaces by means of laser spectroscopic diagnostics

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Abstract – Since the laser discovery, the use of this type of sources became more and more widespread for spectroscopic application relying on their peculiar properties (intensity, monochromaticity, low divergence). Interest arose for in situ characterization of multi-elemental and multilayered surfaces utilized in different fields. To this respect Laser Induced Fluorescence (LIF) and Raman Spectroscopy permit the identification of functional groups at the surface, whenever they emit fluorescence radiation upon UV excitation or present Raman active vibrations as a consequence of the laser induced change in polarizability, respectively. Conversely the elemental composition of the surface and sub-surface layers can be obtained by Laser Induced Breakdown Spectroscopy (LIBS), in a micro-destructive characterization. Applications relevant to micro-analysis with imaging capabilities have been quickly developed for the considered laser spectroscopies. The laser Diagnostic and Metrology Laboratory at ENEA Frascati carried out the development of laser based spectroscopic systems for remote use in the field of environmental, Security, forensic and Cultural Heritage characterization. Recent achievements in the latter case will be presented as examples of technological solution and data analysis procedures for the complex problems encountered.

Keywords: LIF, LIBS, Raman, imaging, remote analysis, stratigraphy

Riassunto – *Caratterizzazione remota di superfici multistrato mediante diagnostiche laser spettroscopiche*. In diversissimi ambiti, da quello industriale a quello dei beni culturali, è sempre più sentita la necessità di diagnostiche accurate minimamente invasive su superfici a multistrato per applicazioni che spaziano dai controlli di qualità di prodotti tecnologici alla caratterizzazione e datazione di reperti del passato. Alcune tecniche laser spettroscopiche, sfruttando le caratteristiche della sorgente (intensità, monocromaticità e focalizzabilità) in combinazione con sistemi di scansione ad alta risoluzione spaziale consentono di ottenere informazioni relative alla distribuzione di elementi e gruppi funzionali su una superficie e anche attraverso gli strati sottostanti della medesima. In particolare la Spettroscopia di Fluorescenza Indotta da Laser (LIF) e la Spettroscopia Raman forniscono informazioni sui gruppi funzionali presenti, nel primo caso se caratterizzati da emissione di fluorescenza sotto eccitazione ultravioletta, nel secondo se Raman attivi su specifiche vibrazioni a seguito della variazione di polarizzabilità indotta dal laser medesimo. La Spettroscopia di Breakdown Indotta da Laser (LIBS) invece consente l'identificazione delle specie atomiche presenti sulla superficie ed una stratigrafia microdistruttiva ad alta risoluzione. Tutte e tre le tecniche spettroscopiche citate sono state sviluppate per applicazioni di imaging anche all'interno di un microscopio (microanalisi). Nonostante la difficoltà di ottenere dati quantitativi accurati nel caso di campioni multistrato complessi, queste tecniche hanno suscitato un crescente interesse per la loro versatilità e le prospettive di sviluppare sistemi di analisi trasportabili da utilizzare in situ, al di fuori dei laboratori di ricerca (ad esempio in ambienti industriali o estrattivi). L'utilizzo di intensi fasci laser in combinazione con sistemi telescopici ha anche reso possibile la realizzazione di sistemi analisi remota delle superfici medesime, qualora non fossero avvicinabili. Il laboratorio di Diagnostiche e Metrologia dell'ENEA di Frascati si è specializzato nello sviluppo di questa ultima tipologia di sistemi laser per applicazioni ambientali, di Security e forensi, e per la caratterizzazione di superfici decorate di Beni Culturali inamovibili. Nel presente contributo verranno discusse le soluzioni tecniche e le procedure messe a punto per l'utilizzo remoto delle tecniche spettroscopiche citate e verranno forniti alcuni recenti esempi di applicazioni relative ai Beni Culturali.

Parole chiave: LIF, LIBS, Raman, analisi d'immagine, analisi remota, stratigrafia

Introduction

Multilayered surfaces requiring a careful characterization in composition are very often encountered in common life, ranging from industrial coatings to decorated surfaces relevant to Cultural Heritage (CH). In the latter case the problem of surface characterization is very often worsened due to the conservation status of the artifact, that may have suffered from aging due to both physico-chemical and biological agents and to the environmental conditions for findings in archaeological areas. Spectroscopic techniques, with minimally invasive optical sampling, resulted to be very suitable to deal with these problems, especially when implying laser interrogation of the surface [1].

The monochromatic laser beam interaction with a surface may cause different phenomena, with a probability depending on the incoming power for surface unit (irradiance), which determines the final energy balance. To the development of suitable spectroscopic diagnostics based on the laser interrogation of the surface, some simple mechanisms can be schematized at different laser irradiances, as shown in Fig. 1. Together with partial radiation absorption, at growing irradiance, we may have:

- Back Scattering (BS) at the same wavelength as the exciting beam;
- Laser induced Fluorescence (LIF) at wavelengths larger than the incoming (UV-VIS) one. Observed shifts are relevant to energy differences between electronic states, eventually coupled through internal relaxations processes in species at the surface [2];
- Stokes Raman Scattering (SRS) also at wavelengths larger than the incoming one, with shifts related to vibrational modes in the species at the surface [3].

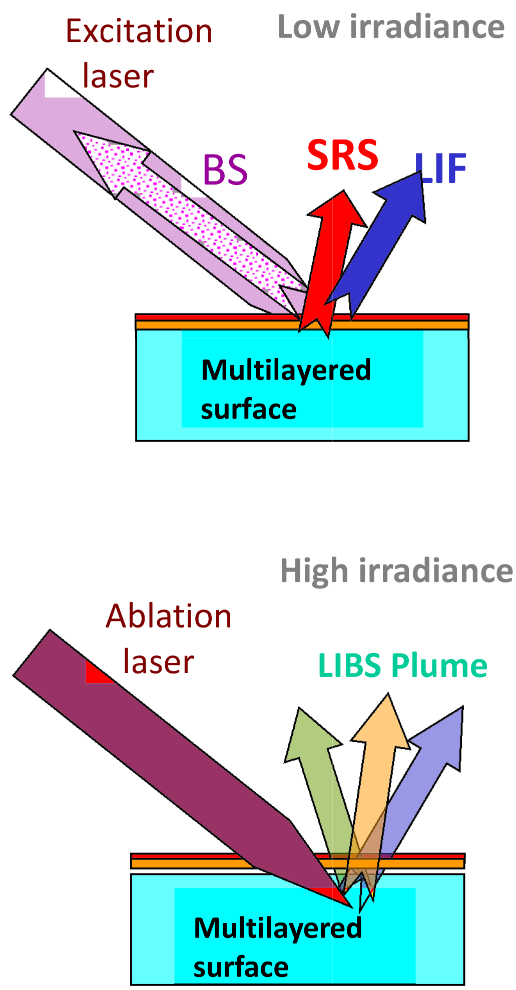

Fig. 1. Schematic of laser interaction with a multilayered surface: at low laser intensity (top) and at high laser intensity (bottom), respectively. See the text for acronym definitions.

Once the ablation threshold is overcome (typically above ~1 GW/cm^2), the surface starts vaporizing and ionization in the ejected material originates a plasma plume, then we have:

- Laser Induced Breakdown (LIBS) with atomic emission from the plasma generated at the surface [4].

Instrumentation

The Diagnostics and Metrology Laboratory at ENEA Frascati developed several patented prototypes for remote application of the mentioned spectroscopic techniques. In most cases operating in spectral and time resolved mode and with imaging capabilities. Depending on the foreseen application and the scenario's requirements, different instruments could implement either a single spectroscopy for a fast data analysis or a combination of the three for a complete surface characterization.

The LIF-art prototype with spectral and time resolved operation modes and imaging analysis capabilities, belongs to the first group. The ILS (Integrated Laser Sensor) prototype, with LIF, LIBS and Raman remote capabilities, belongs to the second group. They are both shortly described in the following.

1. LIF-art prototype

The hyperspectral LIF-art prototype, shown Fig. 2, is equipped with a pulsed Nd:YAG laser operating at 266 nm as excitation source (1.5 mJ energy/pulse, 8 ns pulse duration, 20 Hz repetition rate). A spectrometer (Jobin-Yvon CP240) allows collecting the light in the range of 190-800 nm. The laser spot is focused on the target by a quartz cylindrical lens, resulting in a linear blade of light, allowing for a fast scanning linear sections of the target instead of successive single point interrogations. The one dimension focusing has the advantage to drastically reduce the energy at each target point, thus avoiding any damage risk at the examined surface. The ICCD detector (ANDOR iStar DH734) is mounted behind a slit parallel to the laser line footprint during the scanning. Time resolved LIF measurements are implemented by modulating the trigger signal of the CCD intensifier. At each selected time gate, the entire spectrum is acquired in the selected monochromator range. This prototype is completed by its customized software with algorithms for image processing based on Principal Component Analysis (PCA), Multiple Curve Regression (MCR) and SAM (Spectral Angle Mapper). The automatic extraction of features relevant to conservation problems, such as location of bio attacks, of former consolidants and retouches, of discoloration and detachments can be performed. LIF-art was designed for remote diagnostics on CH surfaces and successfully *in situ* applied on frescoes since its first campaign [5].

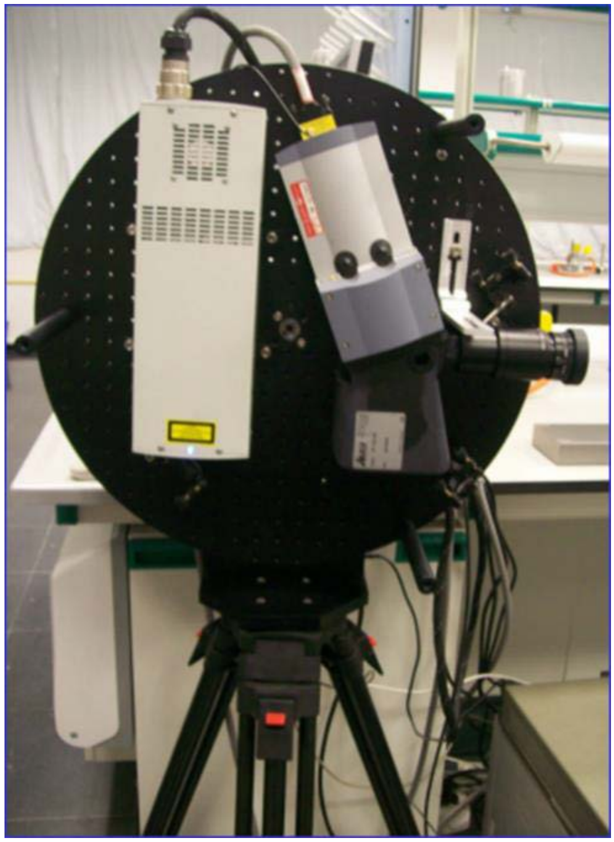

Fig. 2. Picture of the LIF-art prototype. The rotating wheel for the line scanning hosts both the laser source (left) and the ICCD detector (middle); on the right the optics holder.

2. The ILS prototype

The ILS prototype, shown in Fig. 3, was developed during the FP7 project EDEN (End-user driven DEmo for crbNe) for stand-off laser spectroscopy measurements up to 100 mm distance and outdoor tested up to 30 m [6]. For LIF and Raman measurements the excitation source operates at 355 nm (230 mJ/pulse), while LIBS signal is generated by the near IR radiation at 1064 nm (850 mJ/pulse, 6 ns pulse duration, 10 Hz repetition rate), both wavelengths come from the same high energy laser source (Quantel, Q-Smart) coupled to a home-built wavelength multiplier. LIF and LIBS signals are directed towards a large core silica fiber and brought to an Echelle spectrometer (Andor, Mechelle 5000), covering the 200-900 nm range and equipped with an ICCD camera (Andor iStar DH334T). The weakest Raman signal is detected selecting another channel where a fiber bundle is coupled to a Czerny-Turner spectrometer (HORIBA, iHR-320) equipped with a CCD detectors (Andor, iKon M934). The switching between the laser wavelengths and the spectroscopic techniques is fully automatic in less than 10 sec. The protype is equipped with an autofocus device for performing scans on the target area along a chosen grid at selected laser intensity.

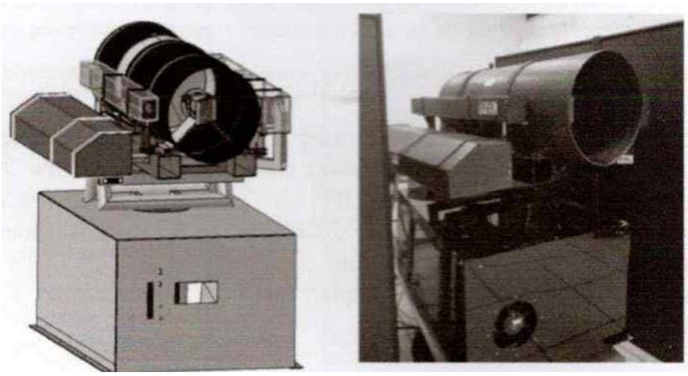

Fig. 3. Schematic (left) and picture (right) of the ILS prototype. The laser (top-left) and the telescope (top-right) are placed above the monochromator.

It can be controlled via wireless communication. Nevertheless, the prototype was designed for Security and forensic applications, applications on CH surfaces were obtained at a distance in laboratory on painted reference specimens [7] and pre-Colombian Mexican ceramic samples [8].

Results and discussion

Remote applications of ENEA laser spectroscopic prototypes were demonstrated during recent Regional projects addressed to technology transfer in the field of CH conservation, such as C.O.B.R.A.[a] and A.D.A.M.O.[b] funded by Regione Lazio, the latter within DTC[c]. Specifically, the LIF art prototype was utilized in archaeological area (necropolis [9], catacombs [10]) and museums on painted surfaces and marble statues. ILS remote laboratory characterization of ceramic was continued examining Italic samples. A few significant examples of achievements obtained by the instruments are reported and discussed in the following.

1. LIF-art applications

The minor Basilica of S. Nicola in Carcere in Rome is a XIth century church built nearby the Tiber river bed, which suffers of major problem related to humidity infiltration. For this reason, its walls had to be periodically repainted and measures were periodically taken to counteract the effect of water infiltration. Within the

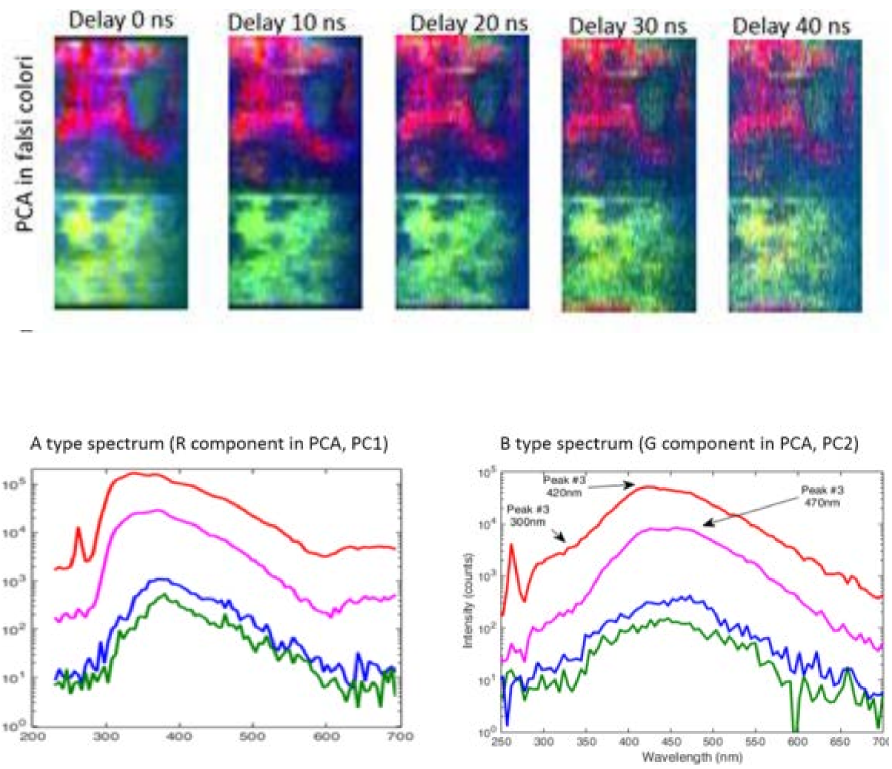

Fig. 4. Top: TG images of a section of the chorus with large (lower) and small (upper) degradation. Bottom: the respective spectra after PCA deconvolution.

ADAMO project a multidisciplinary group of researchers was involved in in-situ measurements addressed to establish the amount of water infiltrations in the chorus [11] and to characterize the last fresco on the apse dome [12], painted by Vincenzo Pasqualoni in the XIXth century.

The ENEA LIF-art prototype was used to collect florescence images excited at 266nm (integration time 1 s, irradiance 5μJ/cm²). RGB false color images reconstructed on the chorus at 560, 420 and 330nm, contained direct information about biodegrading agents (@330 nm), in contrary saline effluorescence and depigmentation originated an increased emission from the calcite substrate (@420 and 560 nm). Time Gated (TG) fluorescence images were collected at two different parts of the chorus, showing respectively intense (A) and weak (B) biodegrading presence. The image and the relevant spectra corresponding to PC1 and PC2 component of PCA are reported in Fig. 4. Results clearly show the possibility of distinguishing the two cases in the spectral range examined, also different time decay constants were observed.

ENEA LIF-art prototype was used, with the same laser parameters but at lower irradiance (2μJ/cm²) on the fresco at the dome to identify and locate former restoration interventions. In Fig. 5 (top left) the RGB fluorescence image reconstructed at 560, 420 and 330nm is shown. Evidence for ZnO retouches and use of paraloyd as consolidant was found in the PCA analysis. The precise location of the ZnO retouch (top left) was obtained by SAM projection of its reference spectrum (bottom) onto the image. Analogously the paraloyd consolidant, associated to the 420 nm band, was evident in the blue area at the bottom right of the LIF image. The TG analysis of the bands confirmed the different time decay constant of ZnO and paraloyd with respect to the calcite substrate.

The ENEA LIF-art prototype resulted to be very suitable to the characterization of marble statues, since the natural $CaCO_3$ impurities resulted to be responsible for differences in fluorescence signature of marbles from different historical caves [13]. A detailed study was carried out at the Altemps Palace Museum in Rome, where a collection of Roman marbles, restored in the Renaissance period, is available. A picture of LIF-art prototype scanning details the ARES statue is shown in Fig. 6 (top), relevant to the RGB reconstruction carried out at 310, 500, 600 nm. Results collected on the foot show the occurrence of a Renaissance integration with a different type of marble (Carrara) with respect to the statue body

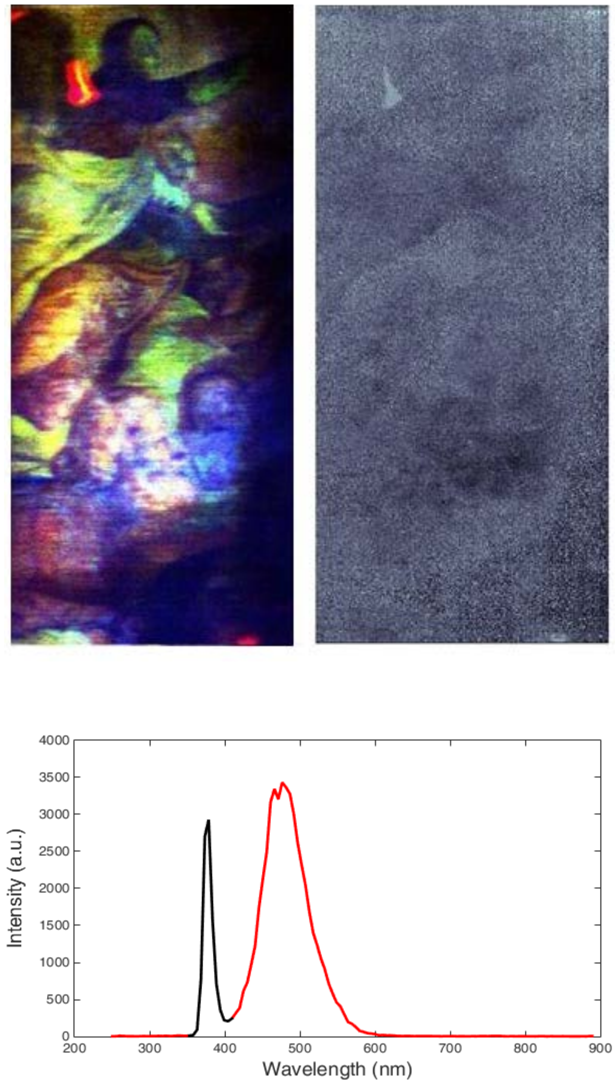

Fig. 5. Identification and distribution of retouches and consolidants on the fresco. Top: False color LIF image at 0 delay (left), SAM projection of the ZnO spectrum (right). Bottom: reference spectrum of ZnO (peaked at 380nm) on plaster.

from the Greek marble (penthelic) used in Roman times. The false color image shown in figure 6 (bottom), shows the difference in fluorescence between the two types of marbles. Furthermore, the fluorescence spectrum (collected in the red ellipse area) revealed the use of ZiO (peaked at 380 nm) to whiten the junction between the different marbles.

2. ILS application

The importance of remote characterization of ceramic relies in their wide-spread use on buildings in the

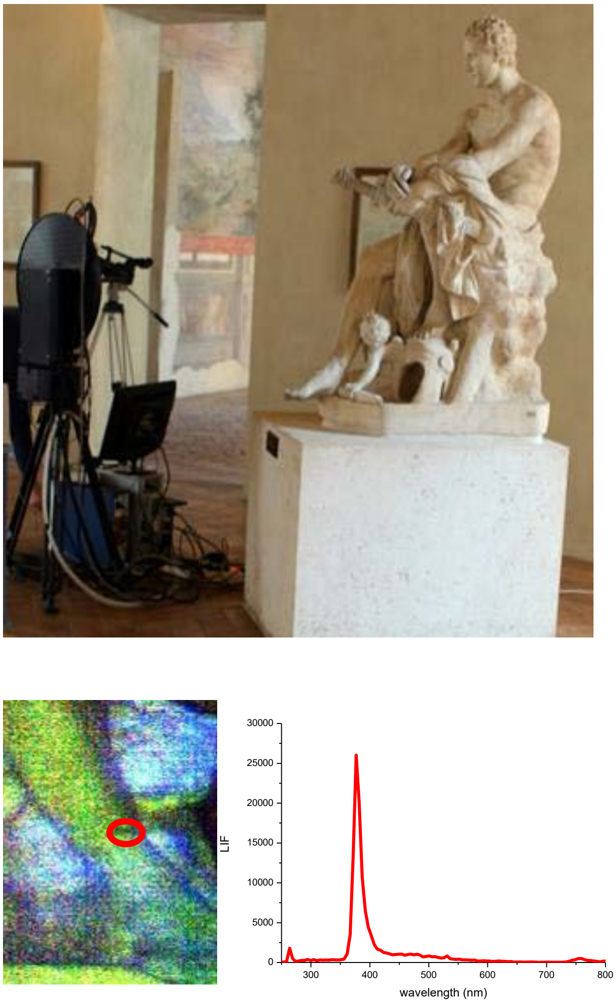

Fig. 6. Top: LIF-art scanning the ARES in Ludovisi's collection at Palazzo Altemps. Bottom: LIF image collected, showing different fluorescence band in the leg and the foot (left); spectral signature of ZnO detected at the junction (right).

Mediterranean area since antiquity and Middle age. Within COBRA project the ENEA ILS prototype was utilized in laboratory at 9,5 m distance for the remote LIBS characterization of ceramics from a *butto* near Tarquinia containing samples from the XIIIth to the XIXth century [14]. The laser radiation at 1064 nm (400 mJ energy/pulse, 2Hz repetition rate), was focused onto the target at a fluence of 13 J/cm^2. The LIBS signal generated was collected thought the telescope and focused onto the ICCD detector. An example of the characterized samples is shown in Fig. 7 (top), where the picture of one of the examined samples is shown as collected though the Cassegrain telescope. Results of the qualitative analysis are reported in Table 1, while the stratigraphy on the most important elements in shown in Fig. 7 (bottom).

Table 1 – Qualitative LIBS analysis of the ceramic sample displayed in fig. 7 top.

glaze	white	blue	yellow	brown
Cu, Ag, Al, Ca, Mg, Mn, Fe, Sr, Na, Li, K	Cu, Ag, Pb, Sn	Cu, Pb, Si, Al, Mg	Cu, Ag, Mg, Mn, Li, K, Rb	Cu, Ag

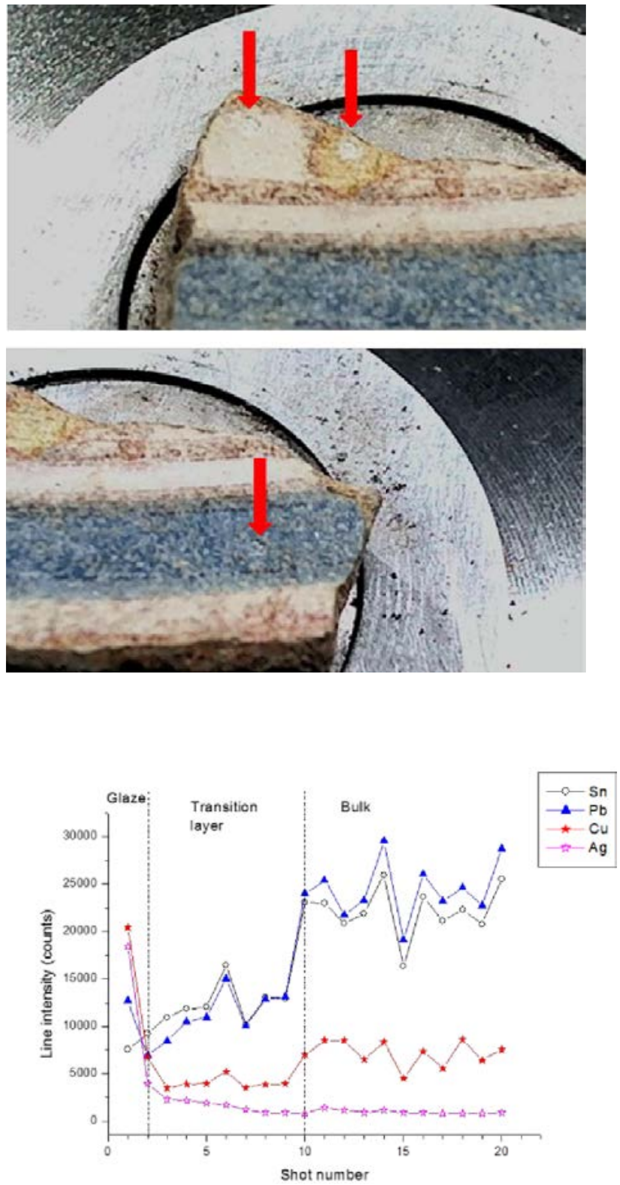

Fig. 7. Top: picture of one examined sample, arrows mark the point where the LIBS signal was collected, small crater can be seen; Bottom: LIBS spectra at the different sampling points.

LIBS results have demonstrated that the blue pigment is a cobalt based smalt, probably saffre made starting from a complex Co–Ni–Fe–As ore. The stratigraphy shows in the first layer a copper/silver rich glaze, and that the same elements are dominant in the yellow luster. The latter observation suggests the possible dating to this fragment in the XVIth century [15], according to Piccolpasso receipt for pottery.

Conclusions

The present paper has reported, with a few significant examples, the fruitful use of remote applications of laser spectroscopies on CH samples. Nevertheless, the needs for reference materials and calibration, both LIF and LIBS qualitative and semiquantitative data collected could supply in a minimally invasive manner valuable information about the sample composition, provenance and dating.

Acknowledgement

All authors wish to remember in this note the initial contribution to the laser remote diagnostics development given by Prof. Anna Giardini, who was in the '80ies the first director of the Molecular Spectroscopy and Laser Application Laboratory at ENEA Frascati. She promoted the use of laser sources both for material processing (laser isotope separation and photochemistry) and spectroscopic diagnostics (laser induced fluorescence, multiphoton ionization, photofragments spectroscopy). The Laboratory, with its staff of researchers and technician was addressed to design, build and successfully operate prototypes. The successive development of the Laboratory towards different applications was to a certain extent a natural consequence of her vision. After her time at ENEA a fruitful cooperation with her University and CNR groups were established along joint National projects addressed to laser driven nanotechnologies and Cultural Heritage conservation.

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Footnotes (Project Acronyms)

(a) COBRA (Development and dissemination of advanced methods, technologies and tools for the Conservation of Cultural Heritage, based on the application of Radiation and Enabling Technologies).

(b) ADAMO (Technologies of analysis, diagnostics, monitoring for the conservation and restoration of cultural heritage).

(c) DTC (District of Technologies for Culture)