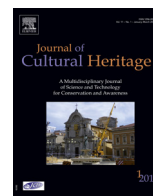




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Original article

Analysis of heritage stones and model wall paintings by pulsed laser excitation of Raman, laser-induced fluorescence and laser-induced breakdown spectroscopy signals with a hybrid system

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ARTICLE INFO

Article history:

Received 22 December 2017

Accepted 7 February 2018

Available online xxx

Keywords:

Hybrid system

Raman spectroscopy

Laser induced fluorescence

Laser induced breakdown spectroscopy

Cultural heritage

ABSTRACT

Analysis of heritage stone samples, alabaster, gypsum, limestone and marble, and model wall paintings was carried out with a laboratory, hybrid system based on the pulsed laser excitation of Raman, laser-induced fluorescence and laser-induced breakdown spectroscopy signals. The system is based on a nanosecond Q-switched Nd:YAG laser operating at its second (532 nm), third (355 nm) and fourth (266 nm) harmonics and a spectrograph coupled to a time-gated intensified charge coupled device for spectral analysis allowing detection with temporal resolution. For the stone samples, Raman spectra display the characteristic vibration modes of SO_4^{2-} of calcium sulfate, in alabaster and gypsum, and of free CO_3^{2-} of calcium carbonate, in limestone and marble. Simultaneously acquired laser-induced fluorescence spectra reveal characteristic bands that help to distinguish between heritage stone types. The elemental composition of stone samples is obtained by laser-induced breakdown spectroscopy upon excitation at 355 nm. Spectra of all stone samples reveal their elemental composition that includes Ca, Na, Mn and Sr and the presence of molecular species, such as CN, C_2 and CaO. Additional emission lines, ascribed to Mg, Si, Al and K, appear with different intensities according to the nature of the stone material. Model wall paintings, based on a red pigment, prepared as fresco or mixed with two different binders, were also studied. The complementary information provided by the three spectroscopic modes allows the identification of the pigment as red vermilion and of the different preparations based on the pigment alone or in mixtures with linseed oil and egg yolk binders.

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1. Introduction and research aim

Laser spectroscopies, such as Raman, laser-induced fluorescence (LIF) and laser-induced breakdown spectroscopy (LIBS) are widely used for analysis of materials and substrates of cultural heritage [1–12]. Raman and LIBS have been commonly used together as they provide complementary information on molecular and elemental composition respectively, and in several studies, this combined approach has led to the integrated characterization of pigments and minerals [13–17]. Raman spectroscopy yields information on superficial molecular composition and has become an important technique in the investigation of archaeological and artistic sub-

strates and objects [8,9]. Raman signals are usually collected upon excitation with a continuous wave laser, but the use of pulsed laser excitation becomes possible by using intensified charge coupled device (ICCD) cameras synchronized with the laser pulse for signal acquisition. In this case, by applying a short temporal gate, it is possible to discriminate the Raman bands from other contributions, including luminescence and background scattered light [18–20]. LIBS involves the ablation of a minute quantity of material, ejected as a micro plasma from the surface sample, and requires the excitation with a focused pulsed laser [1–6]. LIBS has been used in a wide variety of analytical applications for the qualitative, semi-quantitative and quantitative analysis of materials and offers specific features of particular relevance in the context of analysis of cultural heritage materials [1,2,10–12]. A recent work has shown the effect of laser excitation wavelength on the analysis by LIBS of painting samples, concluding that short wavelengths favour the characterization of this kind of substrates [21].

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The implementation of a hybrid concept, combining Raman and LIBS techniques, allows interrogating samples using pulsed laser beams with identical characteristics. In the last years, several instruments with Raman and LIBS capabilities based on a pulsed source, generally using different harmonics from a Q-switched Nd:YAG laser (fundamental emission at 1064 nm), have been developed [22–33]. These systems have been used in the context of cultural heritage [22–25], standoff analysis of explosive materials [26], analysis of geological samples [27,28], etc., and some prototypes have been reported in relation to planetary missions [29–33]. Ref. [34] provides a review of basic instrumental principles, design requirements and technological aspects of the combination of Raman and LIBS.

The combined use of Raman spectroscopy and LIBS serves the purpose of identifying the constituent materials in inorganic samples. However, when dealing with organic substrates, the frequent presence of fluorescent emissions can mask the Raman signals [22]. In these cases, LIF spectroscopy provides complementary analytical information [3,7,35–38] and, due to its high sensitivity, facilitates the detection of trace species. Integrating LIF capabilities with Raman and LIBS has shown to be particularly advantageous for the analysis of cultural heritage materials [7]. Efforts have been devoted to develop hybrid setups based in a common pulsed laser source capable of in situ recording Raman, time-resolved remote LIF, and LIB spectra from the same spot of a substrate or of an object [39,40]. The results of those investigations have shown that a combination of time-resolved Raman and LIF spectroscopies with LIBS can be effectively used for detecting various types of phytopigment biomarkers on planetary surfaces. More recently, Osticioli et al. [41] have presented a compact instrument capable of recording Raman, LIB, and LIF spectra with capacity to provide complementary information regarding the substrate chemical composition. In the case of cultural heritage substrates, it has been shown that time-resolved measurements of luminescence signals is advantageous, as it provides additional, useful information of the origin of fluorescence bands, allowing identification of trace organic substances [42].

In this work, we present the analysis of heritage stones, alabaster, gypsum, limestone and marble, and model wall paintings based on a red pigment, with a hybrid system that allows acquisition of Raman, LIF and LIBS signals from the same sample spot. In such system, the single Q-Switched Nd:YAG excitation laser delivers nanosecond pulses and operates at its second (532 nm), third (355 nm) or fourth (266 nm) harmonics. We aim at the validation of the developed system and at the determination of the optimum

excitation laser wavelength and detection parameters, including spectral and temporal ranges, allowing the identification of the type of minerals in the stone samples and the characterization of the pigment and binder composition in the wall paintings.

2. Methods and materials

Measurements were performed with a laboratory compact hybrid Raman, LIF and LIBS setup that is schematized in Fig. 1. It is based on the excitation of the three types of spectroscopic signals with a Q-Switched Nd:YAG laser (LS-2147, Lotis II) operating, as mentioned, at 532, 355 or 266 nm, at a repetition rate of 10 Hz and delivering pulses of 17 ns with Gaussian-like spatial profile. The linearly polarized laser beam is directed to the surface of the sample by means of dichroic mirrors at an incidence angle of 45°. The mirrors are mounted in a turret, making mirror changes an easy task, and reducing the time required to pass from one irradiation wavelength to another. For LIBS measurements, and to increase the laser fluence values above the ablation threshold of the material analysed, the laser beam is focused with a spherical plano-convex quartz lens (L1), with a focal length of 150 mm, placed in a flip mount and inserted in the beam path in front of the sample. A diaphragm (D) is used to control the size of the sample surface illuminated by the laser. The laser pulse energy can be varied with a variable dielectric attenuator (Laser Optik). The average pulse-to-pulse energy fluctuations are of the order of 10%. The laser spot size and pulse energy are adjusted to their lowest possible values, to achieve the maximum superficial resolution, to avoid sample damage and to obtain spectra with a high signal to noise ratio. Particularly, for Raman and LIF measurements, the laser spot diameter and the fluence value were of 2 mm and 20 mJ cm⁻², respectively, for the three used wavelengths. For LIBS, the laser spot diameter was 200 μm for the three irradiation wavelengths and the fluence values were 6 J cm⁻², for irradiation at 266 and 355 nm, and 10 J cm⁻² for irradiation at 532 nm.

Raman, LIF and LIB spectra were acquired using a 0.30 m focal length spectrograph (TMC300, Bentham) equipped with two interchangeable diffraction gratings, both blazed at 500 nm, with 1200 and 300 lines mm⁻¹, that provide a spectral coverage of 50 and 280 nm, respectively in the 250–650 nm region. The spectrograph entrance slit width values were 50 and 500 μm, for the 1200 and 300 lines mm⁻¹ diffraction gratings, respectively. The spectrograph is coupled to an ICCD (DH-501, Andor Technologies) operated in the gated mode by means of a digital delay/pulse generator (DG-535,

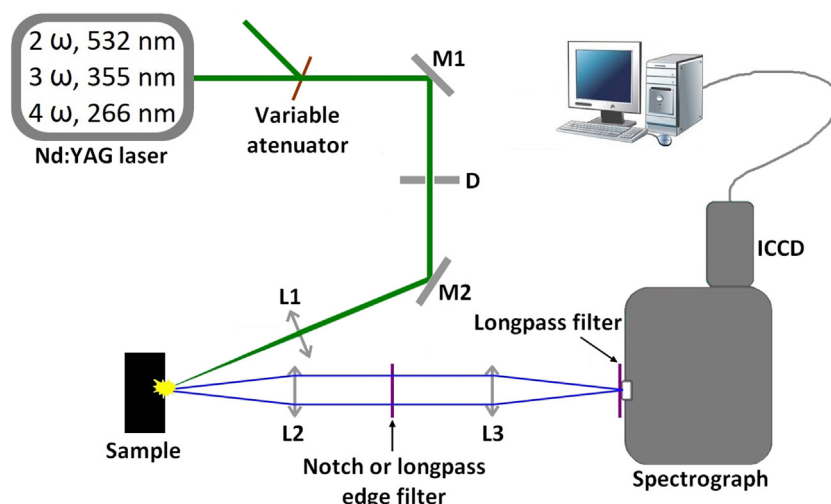


Fig. 1. Scheme of the Raman-LIF-LIBS setup. M: mirror, D: diaphragm, L: lens, ICCD: intensified charge coupled device.

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