

LIF-Raman-LIBS analysis of heritage stones with a single set-up using UV pulsed laser excitation

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Laser based analysis of artworks benefits from the development of hybrid instruments where a single laser source serves to excite fluorescence, Raman and laser induced breakdown spectroscopy (LIBS) signals [1, 2 and refs. therein]. With UV excitation it becomes possible to collect LIF spectra of a wider range of materials, thus allowing the combined acquisition of LIF, Raman and LIBS signals with a common excitation wavelength in a single set-up. Here, we present results obtained upon excitation at 355 nm, third harmonic of a Q-switched Nd:YAG laser. The system includes appropriate optics for beam delivery and signal collection, with Notch and cutoff filters to reject laser scattered light, and a spectrograph (300 or 1200 lines/mm gratings) coupled to a time-gated intensified charge coupled device for spectral analysis and detection with temporal resolution. With this system we have collected the three signal modalities from heritage stone samples of alabaster, limestone and marble.

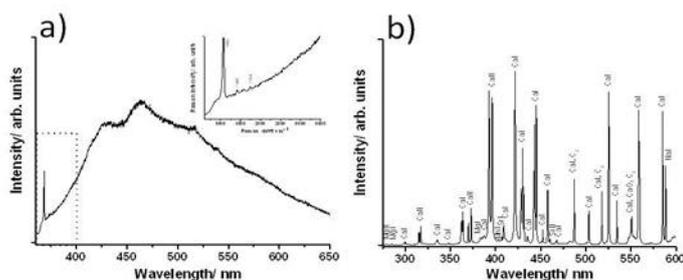


Figure. Spectra acquired on Hontoria limestone upon common laser excitation at 355 nm in a single set-up. a) Raman-LIF spectrum, inset in a) represents the area within the dotted square as a function of the Raman shift, and b) LIBS spectrum with assignment of lines.

As an example, the figure shows spectra acquired on a limestone sample of the Hontoria variety (Burgos Museum, Spain). The LIF and Raman signals are collected together in a single spectrum that consists of two main broad fluorescence bands, centered at 425 and 475 nm, and sharp Raman peaks. The fluorescence bands are assigned to acid-extractable organics and bitumen [3], main limestone fluorophores, while the Raman bands are characteristic of calcium carbonate and correspond to a vibration mode of free CO_3^{2-} (1085 cm^{-1}) and organic residues (1445 and 1744 cm^{-1}). The LIBS spectrum reveals the elemental composition of limestone, displaying emissions of Ca, Na, Mg, Sr, Mn, C_2 (Swan bands) and CaO (Green system).

Funding through programs Geomateriales 2 (S2013/MIT-2914) and IPERION-CH, Ref. H2020-INFRAIA-2014-2015 n° 654028 is acknowledged.

[1] D.W. Hahn, N. Omenetto, *Appl. Spectrosc.* **66** (2012) 347.

[2] D. Anglos, V. Detalle in "Laser-Induced Breakdown Spectroscopy: Theory and Applications", S. Musazzi, U. Perini (Eds.), Springer-Verlag, Berlin, Heidelberg, 2014.

[3] M. Oujja *et al.*, *Anal Bioanal Chem* **402** (2012) 143.