Laser-induced damage on cultural heritage materials: a systematic study using laser excitations at 1064 nm and 785nm to define safe boundary conditions for Raman non-invasive in-situ investigations

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Analytical techniques based on intense radiation sources (photons, particles, lasers, etc.) are commonly applied to investigate cultural heritage objects. Concerns have been raised about the effects of these high fluxes of ionizing and non-ionizing radiations on the precious samples: - *are the results of such measurements representative of the sample properties under examination or rather the consequences of the material alteration under high flux radiations leading to misleading data?*
- within the context of non-invasive methods (generally preferred and sustained in heritage science) are these actually fully respecting the integrity of the material?
Motivated by the fact that, although Raman spectroscopy is widely applied in studying cultural heritage objects, only few studies address the issue of evaluating possible laser-induced damages of the materials [1-4] a method to monitor and control radiation-induced alterations when performing Raman measurements by portable devices was developed and implemented for the study of modern paintings.
A systematic analysis of 24 model paints using a portable Raman device equipped with a double excitation laser source- the ordinarily employed 785 nm and the relatively new one in portable devices at 1064 nm- was performed and here discussed. A protocol for a detailed monitoring of the model samples at increasing laser power density (PD W/cm^2) during the Raman measurements was developed in order to define a PD threshold value for ensuring safe experimental conditions for the materials in terms of unvaried spectral properties and not visible damage of the surface at the micro-scale.
The effect of the laser excitation, the optical properties of the colored pigments (phtalo blue and green, red-PR3 and yellow-PY3 pigments), their behavior when diluted with ZnO and $BaSO_4$ as white pigments, and the nature of the binder (acrylic and oil) were evaluated. For the selected number of pigments the determined PD thresholds resulted relatively high and good Raman spectra were also achievable at lower PDs. Nevertheless, the study underlined that in most of the cases the laser damage was not visible by naked eye but only by a microscopic survey that becomes mandatory when performing in situ Raman measurements with portable devices not equipped with microscope cameras. Moreover, a novel approach placing a thermal sensor in the Raman probe for suitably modulating the laser power during acquisitions and thus preventing overheating and alteration of the materials under study [4] was tested on the same samples.
Overall this study underlines the importance of developing approaches aimed at controlling/monitoring any laser alteration events of the investigated materials in order to guarantee safe operational Raman conditions in the full respect of cultural heritage materials but also for the reliability of the spectral data in support of conservation and restoration issues.

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