Spectroscopic assessment of the UV laser removal of varnishes on paint substrates

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The removal/thinning of aged varnishes from easel paintings is a very complex issue, which involves the need of finely-optimized conservation treatments for preserving both the pictorial substrates and the remaining varnish film. To this goal, cleaning techniques based on laser ablation may satisfy these requirements, especially when wavelengths and pulse durations are accurately selected. Recently, with the aim of minimizing photo-thermal, photo-mechanical and photo-chemical phenomena, ultra-short lasers operating in picosecond and femtosecond regimes have been introduced in the field [1-2]. Processing of fresh mastic and dammar varnishes with 248 nm, 500 fs laser pulses results in an improved etched morphology as compared with ns pulses of the same wavelength [1]. Irradiation of shellac at 213 nm with pulses of 15 ns of photo-sensitive tempera paint models covered with shellac allows controlled micrometric removal without affecting the surface morphology and chemical composition of the remaining varnish film and underlying paint layers. However, fs multiple pulse Ti:Sapphire irradiation of films of this varnish at 795, 398 and 265 nm has turned out to be ineffective for removing shellac varnish from egg-yolk based tempera paints [2].

Taking advantage from the latest findings, in the present work we focus on the assessment of the chemical and physical modifications induced by laser irradiation of varnish samples (i.e. dammar, mastic, shellac, mastic-oil) after natural and artificial ageing by using confocal μ-Raman and laser induced fluorescence spectroscopies. We irradiated the varnish films with the fifth (213 nm) and fourth (266 nm) harmonics of a pulsed nanosecond (15 ns) Q-switched Nd:YAG laser. Together with systematic microscopy inspection of the irradiated areas, a significant effort was devoted to the study of the optical properties of the varnish films by means of UV-Vis absorption spectroscopy, which allowed the determination of linear absorption coefficients at the laser irradiation wavelengths used. Single-pulse laser ablation thresholds were measured by applying the spot regression method and processing of the films was carried out using three different scanning speeds that resulted in 1, 5 and 10 laser pulses on each irradiated area.

The obtained results, using fluences well above the single-pulse ablation threshold of the treated varnishes, depend crucially on the irradiation wavelength, the considered varnish and its degree of polymerization. In contrast with the induced modifications resulting from irradiation at 266 nm, that lead to a whitish appearance (indicative of bubble formation) and discoloration of pigments, the promising results achieved at 213 nm emphasize the importance of using a highly absorbed wavelength to finely remove the oxidized uppermost layer of different types of aged varnishes.

[1] Pouli, P., Paun, I. A., Bounos, G., Georgiou, S., Fotakis, C., *Applied Surface Science*, *254*(21), 2008, 6875-6879.
[2] Oujja, M., García, A., Romero, C., de Aldana, J. R. V., Moreno, P., Castillejo, M., *Physical Chemistry Chemical Physics*, *13*(10), 2011, 4625-4631.