# Non-linear microscopies for the assessment of photochemical modifications upon laser removal of varnishes used in paintings

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A challenging issue in the laser cleaning of paintings is the controlled removal of polymerised degraded varnish coatings. By optimization of laser parameters (wavelength, fluence, duration, and number of pulses), and taking advantage of the possibilities of high spatial resolution, accuracy, material selectivity and immediate feedback, it is possible to circumvent the possible side effects on light-sensitive painting materials, including pigments, binders and protective coatings [1, 2 and references therein].

Imaging based on nonlinear optical microscopy (NLM), a technique initially developed in the field of biomedical optics, allows surface mapping and profiling of multi-layer structures (e.g. coatings) and has been proposed as an examination tool for Cultural Heritage studies [3, 4 and references therein]. In NLM imaging, ultrafast laser excitation serves to exploit several nonlinear optical effects that allow high contrast imaging of samples. The common NLM imaging modes of Multi-Photon Excited Fluorescence (MPEF), and Third Harmonic Generation (THG) provide non-destructive accurate determination of thickness within multilayer samples.

In this work we have aimed at determining by NLM the extent and nature of the photochemical damage that could be induced on underlying painting layers by laser removal of varnish coatings, with the final objective of identifying the optimal laser cleaning conditions that produce the minimum collateral damage in painting layers.

The study has been carried out on model samples, where a top varnish (mastic or dammar) layer coats a bottom layer constituted by a doped synthetic polymer (polymetilmetacrilate, PMMA) film, the latter mimicking a paint layer. To determine the in-depth affected region of the doped polymer layer induced by laser ablation of the varnish, we have applied the NLM modalities of THG and MPEF and a number of laser conditions for varnish removal, namely different UV wavelengths and pulse durations. For NLM measurements and ablation studies we have used the experimental set-ups available at the ULF-FORTH Facility in Heraklion. Characterization of the samples by NLM has been complemented by micro-Raman and laser induced fluorescence (using one-photon excitation in a pump and probe configuration) spectroscopic measurements, thus obtaining a complete characterization of the lateral and in-depth chemical and morphological changes following laser removal of the varnish layer.

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[1] Oujja M. el al., Phys. Chem. Chem. Phys. **13** (2011) 4625-4631.
[2] Pouli P. et al., Accounts of Chemical Research **43**(6), (2010) 771-781.
[3] Filippidis G, et al., Microsc. Microanal. **21** (2015) 510–517
[4] Filippidis G, et al., Appl. Phys. A **118** (2015) 417-423.