Comparison between Er:YAG and Nd:YAG laser for the laser assisted removal of degraded protective from stone

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Nd:YAG laser systems (1064 nm) have been widely applied in the removal of protective layers from stone. Many studies have been conducted both on laboratory model samples and real cases, investigating various laser parameters, including pulse duration length. The ability of the Er:YAG laser (2940 nm) to clean stone has mainly been investigated on model samples and for the removal of natural varnishes [1]. We compared the ablation rate, effectiveness and safeness of the laser-assisted removal of synthetic protectives and consolidants from stones using a Q-Switched Nd:YAG laser with different pulse duration and a Er:YAG laser with a pulse duration of 250 µs. Various limestone and sandstone model samples were selected as being representative of the most common stone artifacts subjected to conservative interventions in the past. The consolidants applied were aqueous emulsions of silanes/siloxanes with a low and medium molecular weight (Pulvistop and Idroblock, Geal S.r.l.; and Hydrophase Acqua, Phase Italia) and a Paraloid B72 solution in acetone. The products were applied by brushing to saturation 5x5x2 cm^3 and 10x10x1 cm^3 stone samples. Two sets of laboratory models (one for the Nd:YAG and the other for the Er:YAG laser testing) were then submitted to artificial aging procedures: i) in a Solar Box (CO.FO.ME.GRA 3000e, equipped with Xenon lamp, λ>295 nm) for 400 h at 500 W/m^2, and ii) in a climate chamber with -10/+50°C temperature cycles (Challenge 500, Angelantoni). To evaluate the performances of the materials, the surface changing under ageing and the facility in the removal of products, the following multi-analytical approach was chosen:

- preliminary characterisation of the materials and investigation of the physical properties of the model samples; a Pyroprobe EGA/PY-3030D (Frontier Lab) coupled with a gas chromatograph/mass spectrometer (PY-GC-MS, Agilent Technology) and a portable Fourier transform infrared spectroscopy (FT-IR ALPHA, Bruker) were used to characterize the non-aged products. The water repellence imparted to the laboratory models was tested by means of capillary absorption measurements following the UNI EN 15801:2010 standard. Colorimetry data (using a Minolta ChromaMeter CM-700d) were obtained on various spots of the model samples following the UNI EN 15886:2010 standard;
- all the preliminary tests were performed before and after artificial aging;
- after laser removal of the protective/consolidant, the stone surface was investigated by means of capillary absorption measurements and FTIR analysis. The degradation phenomena were investigated using PY-GC-MS, both on the removed material (after Er:YAG laser application) and on the material left on the stone, which was collected by scalpel on a few selected areas. Finally, environmental scanning electron microscopy (ESEM) was used in order to assess the laser removal efficacy in some tested areas.

Our results highlight that the optimization of the different laser parameters leads to the safe removal of materials used for conservation purposes, which over time have led to yellowing or darkening phenomena on stone artifacts.

[1] D. Ciofini, M. Oujja, M. V. Cañamares, S. Siano, M. Castillejo, Spectroscopic assessment of the UV laser removal of varnishes from painted surfaces, Microchemical Journal **124** (2016) 792-803, doi:10.1016/j.microc.2015.10.031