# Interaction Between Laser Irradiation Nd:YAG (at 1064 nm) and Ultramarine Blue Pigment

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***Abstract.*** *Mural paintings located outdoor are exposed to the action of different deterioration agents that cause, among other forms of deterioration, the formation of superficial crusts. Among the cleaning methods used in cultural heritage, laser ablation is approaching to be a technique capable to ensure a success removal of these crusts, avoiding risks to the historical-artistic value of the substrate. As the literature on laser cleaning of mural paintings is scarce, this study aims to advance in understanding interactions between laser radiation and the pigments of the paintings. In this work, ultramarine blue is irradiated with a nanosecond pulsed Nd:YAG laser operating at 1064 nm and four different fluences. Modifications on colour, chemical composition and micromorphology were evaluated by means of stereomicroscopy, colour spectrophotometry and scanning electron microscopy.*

**Keywords.** Laser, Nd:YAG, pigment, ultramarine blue, laser cleaning, conservation, cultural heritage

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# 1 Introduction

Laser ablation is a physical process based on interaction matter-laser radiation, which in the field of heritage conservation has many applications: chemical analysis, structural diagnostics, optical imaging, and cleaning. In fact, laser cleaning shows a several advantages [1] over other methods, since no additional substances are incorporated, no mechanical contact with the object, it allows precision removal of thin layers of material (contamination, paint, corrosion, etc.), the method is automated and self-controlled and the technique is environmentally friendly.

The pigment ultramarine blue is used as artificial pigment since 1828 to nowadays [2,3], therefore present in many wall paintings. Studies on laser cleaning of paintings are mainly focused on removal of varnishes [4], remains of previous conservation treatments [5], pigments [6], spray paint on stone sample [7]. Due to the difficulty in understanding why some pigments are more susceptible to laser radiation than others, this study aims to investigate what happens to ultramarine blue using a commercial nanosecond pulsed Nd:YAG laser at different fluences operating at 1064 nm.

# 2 Materials and Methods

## 2.1 Ultramarine blue pigment

The pigment ultramarine blue (UL hereinafter) ($3Na_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2Na_2S$) was supplied by Kremer Pigments GmbH & Co, KG (Germany). Pellets of 4 cm diameter and 0.3 cm thickness were prepared in aluminium moulds of 4 cm diameter and compacted with a 30-tonne pressure press.

## 2.2 Laser irradiation

The equipment used in this study was a Q-switched pulsed Nd:YAG laser (Quanta Ray, INDI) operating at 1064 nm. The laser system delivered pulses of 6 ns duration at a constant repetition rate of 10 Hz. The beam reached the surface using a spherical plane-convex lens with a focal length of 250 mm.

Methodology of irradiation was first based on the identification of the fluence at which damages started to become visible on the surface of the sample ($UL_D$). It was decided to lower the fluence starting to induce visible damage 5% to bring it closer to the damage threshold ($UL_{th}$ hereinafter). A fluence 40% above and below $UL_D$ were selected to investigate the effect of the laser on the pellet. A horizontal overlap of 80% and a vertical overlap of 50% were set for each area. Then, four areas of 1.2 cm x 1 cm were irradiated setting 0.4 cm between adjacent irradiations. The following areas were performed:

- Area $UL_D$: fluence of 1.4 $J.cm^{-2}$ and a spot diameter of 0.30 cm.
- Area $UL_{th}$: fluence of 1.3 $J.cm^{-2}$ and a spot diameter of 0.31 cm.
- Area UL-40%: fluence of 0.8 $J.cm^{-2}$ and spot diameter of 0.39 cm.
- Area UL+40%: fluence of 2.0 $J.cm^{-2}$ and a spot diameter of 0.25 cm.

### 2.3 Analytical techniques

#### *2.3.1 Pigment characterisation*

The mineralogical composition of ultramarine blue was determined using X-ray diffraction (XRD, X´Pert PRO PANalytical B.V.). The identification of the minerals was carried out using Xpowder software. The microtexture and elemental composition was studied by means of FEI QUANTA 200 scanning electron microscopy with energy dispersive X-ray spectrometry (EDS) and working in secondary electron (SE) and backscattered electron (BSE) detection modes.

#### *2.3.2 Irradiated areas characterisation*

For the characterization of each irradiated area, the following techniques were applied:

Stereomicroscopy before and after irradiation using an SMZ800 NIKON® to detect the physical changes.

The colour of each irradiated area was characterised using a Minolta CM-700d spectrophotometer obtaining the CIELab and CIELCH colour spaces parameters $L^*$ (lightness), $a^*$ (colour position between red and green), $b^*$ (colour position between yellow and blue), $C^*_{ab}$ (chroma) and $h_{ab}$ (hue) [8]. Measurements were made in specular component excluded (SCE) mode, for a spot diameter of 8mm, using a D65 illuminant and an observer angle of 10°. A total of three measurements for each irradiated area were made. $\Delta L^*$, $\Delta a^*$, $\Delta b^*$, $\Delta C^*_{ab}$ and $\Delta H^*$ colour differences and total colour change ($\Delta E^*_{ab}$) were calculated following [8], taking the data colour of the pellet before irradiation as reference.

Micromorphological and compositional analysis, via scanning electron microscopy (SEM) with energy-dispersive X-ray spectrometry (EDS) using the equipment previously described.

## 3 Results and Discussion

### 3.1 Pigment characterisation

The mineral phases identified by means of XRD in ultramarine blue were the sodalite-group phases such as lazurite (Na3Ca(Al3Si3O12)S) and sodalite (Na8Al6Si6O24Cl2), as well as nepheline (NaAlSiO4) and kaolinite (Al2Si2O5(OH)4). SEM micrographs depicted particles very small in size (1-5 µm) (Fig. 1a) composed, following EDS, of Si, Al, Na and S (Fig. 1b). Additionally, other particles, bigger in size (15-40 µm) and irregular morphology, and composed of Ca and S (Fig. 1c) were found. Kaolinite presence was confirmed by the detection of Al and Si rich particles (Fig. 1d).

### 3.2 Irradiated areas characterisation

By means of stereomicroscopy, morphological differences regarding the fluence per pulse irradiation were found. When the threshold fluence was exceeded, deterioration caused to the pellet by the laser irradiation was more evident, as it became rougher (Fig. 2b) compared to the not irradiated surface (Fig. 2a).

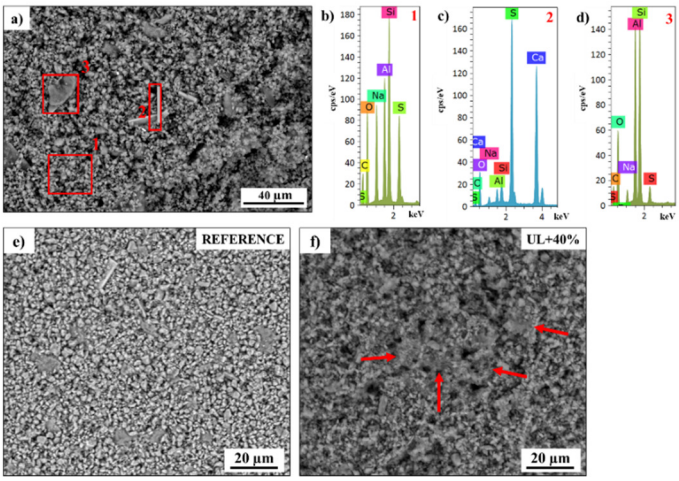


**Figure 1.** SEM micrographs in BSE mode and EDS spectra. (a) micrograph of ultramarine blue pigment; (b-d) EDS spectra of ultramarine blue pigment, (e) micrograph of the not-irradiated area, (f) micrograph of the surface irradiated at the highest fluence with Nd:YAG at 1064 nm; red arrows indicate crust melting.

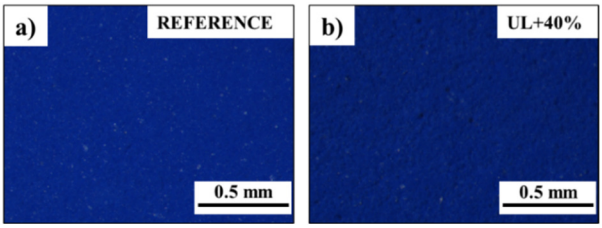


**Figure 2.** Micrographs under stereomicroscopy of some areas of the sample: (a) reference not-irradiated area, (b) UL+40% irradiated area with Nd:YAG at 1064 nm.

Table 1 shows the CIE colour differences and the global colour change ($\Delta E^*_{ab}$) calculated after the irradiation under the four laser conditions. In fact, taking into account the $\Delta E^*_{ab}$, only the colour change produced under UL+40% condition was visible to the human eye, as shown by the $\Delta E^*_{ab}$ obtained for that area, which was higher than 3.5 CIELab units, threshold at which an unexperienced observer can perceive changes in colour [9]. Table 1 also shows that: 1) as the fluence increases, $\Delta E^*_{ab}$ also increases and 2) the colour after UL+40% irradiation tends towards yellow by having positive $\Delta b^*$.

**Table 1**. $\Delta L^*$, $\Delta a^*$, $\Delta b^*$, $\Delta C^*_{ab}$ and $\Delta H^*$ and global colour change ($\Delta E^*_{ab}$) in each one of the irradiated areas. Each value is accompanied by its standard deviation.

| | $\Delta L^*$ | $\Delta a^*$ | $\Delta b^*$ | $\Delta C^*_{ab}$ | $\Delta H^*_{ab}$ | $\Delta E^*_{ab}$ |
|---|---|---|---|---|---|---|
| $UL_D$ | 1.60 ± 0.48 | -1.98 ± 0.68 | -0.54 ± 0.31 | -0.14 ± 0.52 | -2.05 ± 0.74 | 2.61 ± 0.89 |
| $UL_{th}$ | 1.54 ± 0.46 | -1.76 ± 0.65 | -0.58 ± 0.31 | -0.04 ± 0.52 | -1.85 ± 0.89 | 2.41 ± 0.86 |
| UL-40% | 1.24 ± 0.46 | -0.39 ± 0.65 | -1.37 ± 0.31 | 1.15 ± 0.52 | -0.82 ± 0.88 | 1.88 ± 0.86 |
| UL+40% | 1.70 ± 0.49 | -5.73 ± 0.67 | 3.03 ± 0.31 | -4.67 ± 0.52 | -4.49 ± 1.12 | 6.70 ± 0.89 |

SEM allowed to confirm that melting crusts appeared after irradiation at the highest fluence (Fig. 1f comparing with Fig. 1e-not irradiated-).

## 4 Conclusion

Ultramarine blue pigment is susceptible to suffer deterioration by laser irradiation. Irradiated areas experienced greater colour changes as the fluence increased and appeared to become rougher. Fluence of 2 $J.cm^{-2}$ caused a colour change visible to the human eye towards yellowish tones and at the same fluence, SEM showed that crust melting started to appear.

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## References

[1] C. Fotakis, D. Anglos, V. Zafiropulos, S. Georgiou, and V. Tornari, *Lasers in the Preservation of Cultural Heritage*, 0 ed. CRC Press, 2006. doi: 10.1201/9780367800857.

[2] N. Bevilacqua, L. Borgioli, and I. Adrover Gracia, *I pigmenti nell'arte: dalla preistoria alla rivoluzione industriale*. in I talenti, no. 26. Saonara (Pd) [i.e. Padua, Italy]: Il prato, 2010.

[3] O. Casazza, *Il restauro pittorico: nell'unità di metodologia*, 8a ed. Firenze: Nardini, 2007.

[4] D. Ciofini, M. Oujja, M. V. Cañamares, S. Siano, and M. Castillejo, 'Spectroscopic assessment of the UV laser removal of varnishes from painted surfaces', *Microchem. J.*, vol. 124, pp. 792–803, Jan. 2016, doi: 10.1016/j.microc.2015.10.031.

[5] P. Pouli, A. Nevin, A. Andreotti, P. Colombini, S. Georgiou, and C. Fotakis, 'Laser assisted removal of synthetic painting-conservation materials using UV radiation of ns and fs pulse duration: Morphological studies on model samples', *Appl. Surf. Sci.*, vol. 255, no. 9, pp. 4955–4960, Feb. 2009, doi: 10.1016/j.apsusc.2008.12.049.

[6] P. Pouli, D. C. Emmony, C. E. Madden, and I. Sutherland, 'Studies towards a thorough understanding of the laser-induced discoloration mechanisms of medieval pigments', *J. Cult. Herit.*, vol. 4, pp. 271–275, Jan. 2003, doi: 10.1016/S1296-2074(02)01207-4.

[7] C. Giusti, M. P. Colombini, A. Lluveras-Tenorio, J. La Nasa, J. Striova, and B. Salvadori, 'Graphic vandalism: Multi-analytical evaluation of laser and chemical methods for the removal of spray paints', *J. Cult. Herit.*, vol. 44, pp. 260–274, Jul. 2020, doi: 10.1016/j.culher.2020.01.007.

[8] Commission Internationale de l'eclairage CIE S014-4/E:2007 Colorimetry Part 4: CIE 1976 L*a*b* Colour Space, Vienna, 2007.

[9] W. Mokrzycki and M. Tatol, 'Color difference Delta E - A survey', *Mach. Graph. Vis.*, vol. 20, pp. 383–411, Apr. 2011.