S. ACQUAVIVA[1]

E. D'ANNA[1]

M.L. DE GIORGI[1,✉]

A. DELLA PATRIA[2]

L. PEZZATI[3]

Optical characterization of pigments by reflectance spectroscopy in support of UV laser cleaning treatments

[1] Department of Physics, University of Salento, via Arnesano, 73100 Lecce, Italy

[2] C.N.R.-I.N.O.A., via Barsanti, 73010 Arnesano, Lecce, Italy

[3] C.N.R.-I.N.O.A., Largo E. Fermi, 6, 50125 Arcetri, Firenze, Italy

ABSTRACT The study of optical properties of artwork materials is of fundamental importance for laser-based restoration techniques. In this work, reflectance spectroscopic measurements and colorimetric analyses of painted wooden models were performed to discriminate between pigments on the basis of their spectral features. In particular, the spectral reflection factors of different white pigments were recorded with a fibre optics reflectance spectroscopy module, both before and after excimer laser (248 nm) irradiation. Colour data were obtained and monitored with an integrating sphere spectrophotometer and expressed with the CIE $L^*a^*b^*$ colour coordinates. Moreover, the laser-induced morphological changes of the samples were investigated by scanning electron microscopy.

PACS 42.62-b; 61.80.Ba; 07.60.Dq

1 Introduction

The study of pigments and varnishes used in painted artworks is of fundamental importance for conservation purposes. In general, the investigation involves the application of complementary analytical techniques to return the composition of the employed materials and to deduce the pictorial technique followed by the artist, so as to find the most suitable restoration procedures.

Mechanical and chemical restoration interventions may affect the pigments in an undesirable and non-reversible way. Commonly, the control of these traditional techniques is up to the conservator's ability.

Laser technology is greatly eligible as a safe procedure for the conservation, it being controllable and reproducible; it also seems to suit the conservation principle of 'minimum intervention'. Throughout the last decade [1–9] several researches have been carried out about the interaction of laser radiation with different painting materials (varnishes, pigments and media). A preliminary study is mandatory to avoid discoloration and surface damage; this is accomplished to establish the best working conditions and to infer the laser

parameters (wavelength, fluence and pulse length) for a safe procedure.

Reflectance spectroscopy is a powerful and widely accepted tool in support of restoration interventions. It permits the identification of the pigments and the monitoring of colour changes in a non-invasive way [10, 11].

In this work the reflectance spectroscopic technique is used to discriminate among three different kinds of white pigments and to quantify the chromatic alterations they experienced after irradiation with a KrF excimer laser. Systematic measurements were performed on a well-defined set of unvarnished and varnished painted samples.

2 Sample preparation

A representative sample was a layered structure consisting of a flat wooden support covered with a gypsum layer ($\sim 200\,\mu m$) and painted with white pigments embedded into an egg-based binding medium ($\geq 10\,\mu m$). Due to their historical and artistic relevance, three white pigments were selected among those traditionally utilized in wood and canvas artworks. In particular, on the one hand lithopone and zinc white are interesting for their widespread use since the XVIII century; on the other hand, titanium white, although employed only in modern tempera paintings, was included in our investigations because it may help to identify later retouches on ancient artefacts.

Since, traditionally, varnishes were spread over the paintings as a protective layer and to provide colour saturation, thin layers of different varnishes (few tens of μm thickness) were paintbrush laid on some model samples. Among the natural resins, dammar and mastic were considered, whereas Regalrez and Retoucher were the choices among the synthetic varnishes of modern use.

3 Experimental

For the irradiation tests, a KrF excimer pulsed laser (LEXtra 50, Lambda Physik, $\lambda = 248\,nm$, $\tau = 20\,ns$) was used and its beam profile homogenized by an optical system. The areas of interest on the irradiated surfaces were selected through a clear circular (8-mm diameter) aperture. The fluence, F, was tuned with an attenuator, for fixed values of

✉ Fax: +39-832-297499, E-mail: degiorgi@le.infn.it

laser energy and spot size, and its uncertainty was always about 5%.

A fibre optics reflectance spectroscopy (FORS) module (Zeiss MCS-CCD) provided the spectral reflection factor (SRF) of each model. It is a spectrophotometer equipped with a 1044×64 pixels CCD detector with a very low spectral distance of pixels (0.8 nm/pixel) in the 200–980 nm range and a spectral resolution below 3 nm. Its ability to return a large amount of spectral information without any sampling makes its use very appropriate when it is necessary to perform manipulations of the spectra.

All the spectra were acquired in the 330–800 nm range with the 0/45 geometry by using a dome-shaped plastic probe head that accommodates four optical fibres. At the top of the dome the illumination fibre stood at 0.5 mm above the investigated surfaces and cast a light spot of about 4-mm diameter; three fibres, located symmetrically on the side of the dome and forming a $45°$ angle with respect to the vertical axis, collected the back-scattered light at the same radial distance from the centre of the light spot as the illumination fibre.

The very dense data point forming the SRF returned from this spectrophotometer provided detailed information about each pigment variety, both unvarnished and finished with different varnishes.

For each model sample, a comparison was made between the first derivatives of the spectral reflection factors of the same area before and after irradiation.

Another contact spectrophotometer (Minolta CM-2600d) let us record the SRFs that were used to calculate colour coordinates in order to monitor laser-induced chromatic changes of the models. Its 52-mm-diameter integrating sphere allows colour determination in the $d/8$ geometry, based on spectral acquisitions from a 3-mm-diameter circular spot. All the spectra were taken in the 360–740 nm range, every 10 nm, in specular-excluded (SPEX) mode. In accordance with the recommendations of the Commission Internationale de l'Eclairage (CIE), colour data were calculated under the standard illuminant D_{65} and with the colour-matching functions associated with the standard $10°$ observer [12]. Undesired thermochromism effects were limited by working at $22 °C$.

On every sample, 10 spectra were recorded for each area of interest and every single spectral acquisition was the result of an average over five sequences of illumination. This approach helped both to limit the effects of the instability in the emission of the flash lamps and to return estimates of the statistical fluctuations of the colour coordinates.

The CIE $L^*a^*b^*$ 1976 colorimetric space [13, 14] was used to arrange all colour data points. It is a rectangular coordinate system with L^*, a^*, b^* axes where it is possible to describe the differences in lightness ΔL^* (from 0 – black to 100 – white), redness–greenness Δa^* and yellowness–blueness Δb^* (both unbounded) between any two points. The colour difference ΔE^* is expressed with the Euclidean distance

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \,. \tag{1}$$

Microscopy observations were carried out by means of a scanning electron microscope (SEM, JEOL JSM-6480LV operating in low-vacuum mode) to assess the morphological

modifications within the irradiated areas. At the same time the elemental distribution was inferred from energy-dispersive X-ray (EDX) analyses to characterize laser-induced compositional alterations.

4   Results and discussion

Preliminarily, the visible effects of UV pulsed laser radiation on white-painted surfaces were investigated on every model. Even at very low laser fluences, Regalrez and Retoucher layers peeled off; so systematic measurements were completed on natural resin varnished samples.

Figure 1 shows the SRFs of the unvarnished and non-irradiated pigments, obtained with the FORS module. It is evident that titanium white is the most reflective. This spectral feature gives titanium white its well-known excellent covering ability.

It is practical to underline the characteristic behaviours of the three pigments. In fact, titanium white and lithopone are almost indistinguishable in the UV but rather different above their common shoulder wavelength. For the zinc white the shoulder wavelength is lower and, as a consequence, it is more reflective in the UV region.

To emphasize their spectral differences, the first derivatives of the SRF curves were calculated and the output plotted
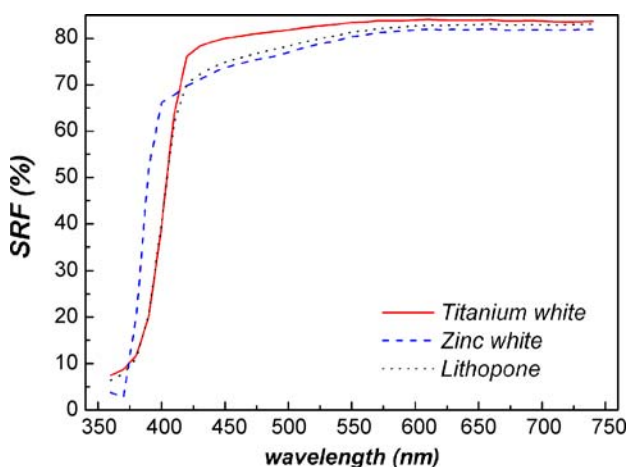

FIGURE 1   SRFs of the unvarnished white pigments

	λ_p (nm)		FWHM (nm)	
	before	after	before	after
Unvarnished				
Titanium	403.1	402.9	20.4	21.1
Zinc	384.2	383.9	8.8	9.2
Lithopone	400.9	400.7	19.2	19.8
Mastic				
Titanium	402.5	402.7	18.5	19.0
Zinc	384.5	384.4	8.7	9.0
Lithopone	401.9	401.8	18.5	18.6
Dammar				
Titanium	403.9	403.7	20.4	21.2
Zinc	384.7	384.4	8.8	9.2
Lithopone	401.5	401.4	18.2	18.3

TABLE 1   Peak wavelengths and bandwidths of the first derivatives of SRFs for every sample, both before and after laser irradiation at the CDT fluence. The uncertainties for λ_p and FWHM values are 0.4 and 0.8 nm, respectively
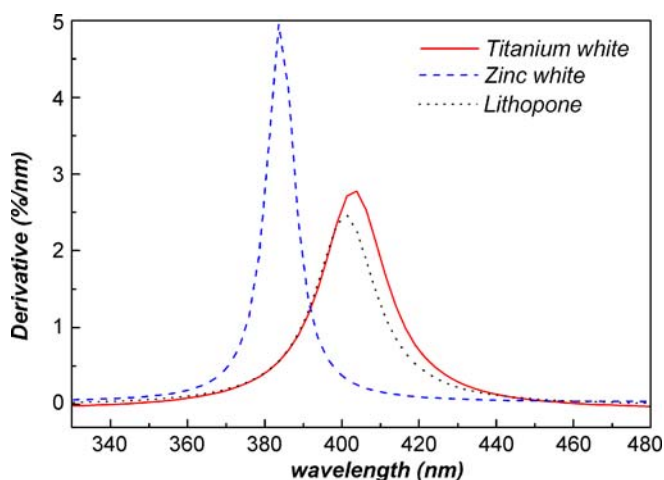
FIGURE 2 First-derivative plot of the unvarnished pigments
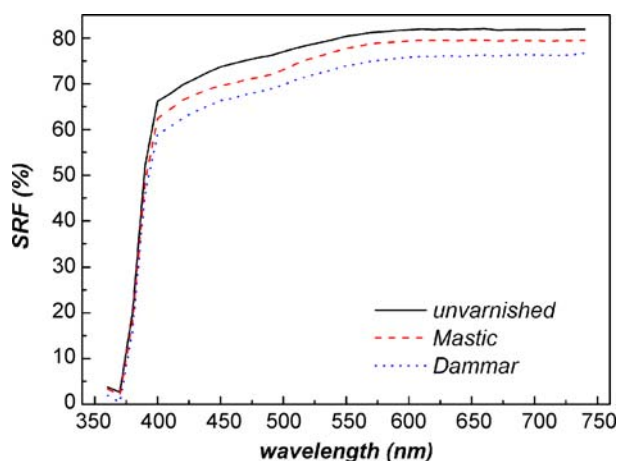

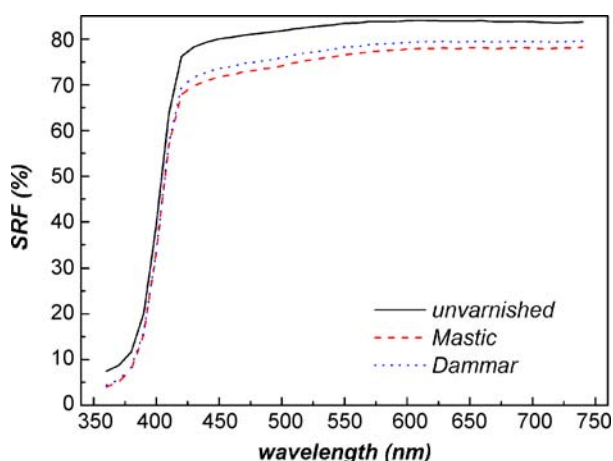
FIGURE 4 SRFs of zinc white models

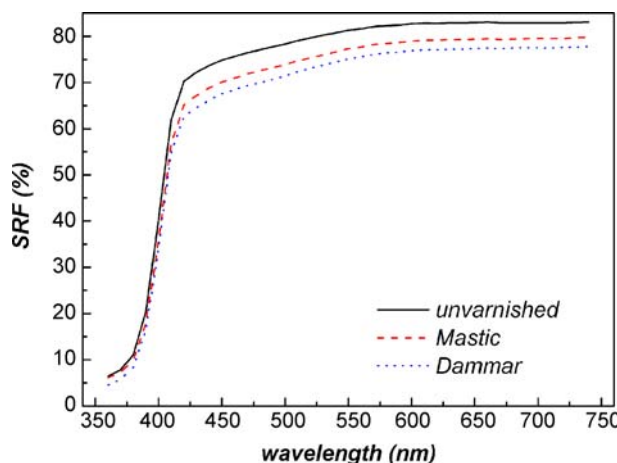
FIGURE 3 SRFs of titanium white models

FIGURE 5 SRFs of lithopone models

in Fig. 2. The wavelengths of the peaks, λ_p, locate the inflection points while the bandwidths, FWHM, characterize the steepness of the SRF curves.

Analogous spectra were recorded for the samples finished with mastic or dammar. Table 1 summarizes the results obtained for both the unvarnished and the varnished surfaces. One can observe that varnishes introduce neither significant λ_p shifts nor FWHM changes.

In order to investigate the chromatic properties of the unvarnished and varnished models, colour coordinates were calculated from the SRF spectra recorded by the Minolta spectrophotometer.

It is worthwhile to point out that the spectral outputs from spectrophotometers working with different geometries are not ordinarily comparable and this is also true for the colour coordinates. Only with the 0/45 and $d/8$ geometries, which involve diffuse reflection excluding the specular contributions, is it possible to obtain almost equal colour differences.

At first, for each pigment the mutual colour differences ΔE^* were calculated between unvarnished and varnished samples, along with the degree of internal colour non-uniformity for every single model, through a colour mapping over 20 regularly arranged areas on each surface. The above-mentioned colour distances arose from the comparison of the mean colour coordinates of the involved samples, while

the internal colour non-uniformity degree was inferred from the mean of the colour differences of every single area with respect to the mean colour coordinates of the investigated sample.

Overlaid graphs of the SRFs of the different models, both unvarnished and finished with mastic or dammar, are shown in Figs. 3–5. In all cases varnish reduces the surface reflectance. Anyway, differently from zinc white and lithopone, the varnished samples of titanium white exhibit an inverse spectral response in the visible region, in that the mastic lowers the spectral reflection factor more than the dammar (with respect to the unvarnished sample). Every noticeable spectral difference between any two curves from these figures is proportional to the corresponding colour distance reported in Table 2.

Afterwards, the models were irradiated at increasing fluence values until a visible discoloration was detected.

	Titanium white	Zinc white	Lithopone
Unvarnished–mastic	3.4 ± 0.2	1.7 ± 0.2	2.0 ± 0.1
Unvarnished–dammar	2.6 ± 0.2	3.2 ± 0.1	3.1 ± 0.2

TABLE 2 Colour distances (ΔE^* units) between models of the same pigment

	Titanium white	Zinc white	Lithopone
Unvarnished	0.5	0.3	0.3
Mastic	0.4	0.8	0.4
Dammar	0.4	0.4	0.5

TABLE 3 Degree of internal non-uniformity (ΔE^* units)

	Titanium white	Zinc white	Lithopone
Unvarnished	60	90	60
Dammar	170	170	170
Mastic	140	170	130

TABLE 4 CDT (mJ/cm^2) values for unvarnished models. The uncertainty was always about 5%

FIGURE 6 SEM micrograph of the dammar-covered titanium white sample after a single-pulse irradiation at CDT fluence. Photograph is taken at the border between non-irradiated and irradiated areas

FIGURE 7 SRFs of (i) unvarnished, (ii) non-irradiated dammar-finished and (iii) irradiated dammar-finished titanium white samples

The next step was the determination of the colour damage threshold, CDT, that was intended to be the fluence at which a single laser pulse induced a significant colour difference with respect to the non-irradiated area. As a rule, this difference is assumed to be meaningful either above unity or above the sample non-uniformity value, if the latter is higher. All the sample models of this work had quite low non-uniformities (Table 3); thus, the value $\Delta E^* = 1$ had to be passed for CDT assessment.

CDT values show different behaviours of the unvarnished and varnished surfaces after laser irradiation (Table 4). At fluences higher than the CDT the irradiated areas showed a clearly visible discoloration. More precisely, the unvarnished titanium white sample turned into a bluish-grey tone, while lithopone and zinc white became dark grey, as already observed by other authors. Nevertheless, these discolorations seemed to be transitory as the samples approached their original colours within about 10 days [3, 6, 7, 9, 15]. The observed laser-induced colour alterations could be due to a modification of the pigment chemical composition through mechanisms of reduction; the return to the original colour could be explained by the reoxidation of the pigment. It is worthwhile to point out that the unvarnished samples were irradiated at fluences that were about one order of magnitude lower than the ablation threshold of the pigments [1].

SRFs from all the samples were acquired after laser irradiation at the CDT fluence, with the aim of inferring if any possible modifications in the derivatives could be related to the minimum noticeable colour alteration. Corresponding λ_p and FWHM values are reported in Table 1.

By comparing the spectral features from the same area before and after laser irradiation, it may be concluded that no significant differences arise, neither in the positions of the peaks nor in the associated bandwidths, and that the induced minimum colour difference does not imply a net modification of the SRF shape.

Colour measurements indicated that laser treatment at moderate fluences (≤ 100 mJ/cm^2) caused small chromatic changes on the surface of the varnished samples; this result suggests that the varnish protects the paint by preventing direct interaction with the UV radiation.

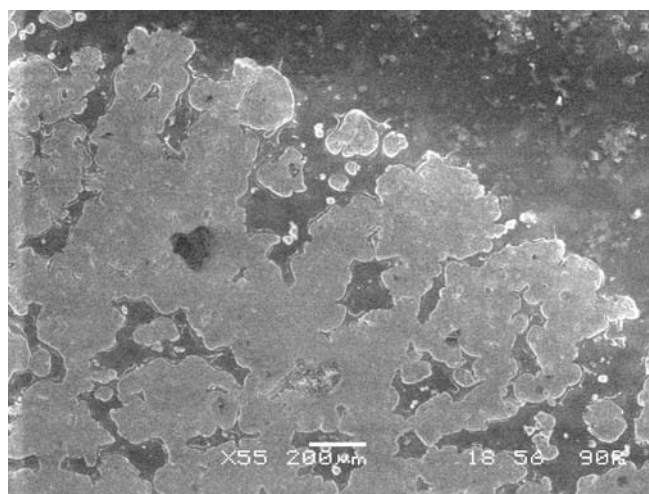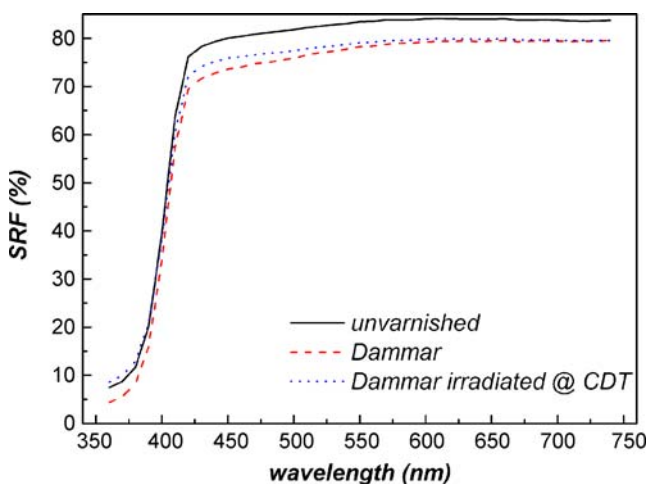Moreover, varnished samples exhibited significant discoloration when the laser fluence was so high as to partially or totally remove the protective layer. The partial ablation of the varnish at the CDT fluence is striking in the SEM micrograph (Fig. 6) of the dammar-covered titanium white sample, reported as an example. In the figure, the bright areas in the irradiated spot witness the varnish removal, as confirmed by EDX analyses, and therefore the reappearing of the original colour.

Analogous results were obtained by SEM and EDX investigations on the whole set of varnished samples irradiated with a single laser pulse at the CDT fluence.

The partial return to the pigment colour is confirmed by Fig. 7 where the SRFs of the (i) unvarnished, (ii) non-irradiated dammar-finished and (iii) irradiated dammar-finished titanium white samples were overlaid. The colour distance between unvarnished and varnished samples decreased after laser irradiation.

5 Conclusions

The efforts of this work were aimed to assess the eligibility of the spectral reflectance technique as a viable

way to the identification of white inorganic pigments and possible retouches on original artworks. The results proved that the technique may serve as support for artwork conservation through the discrimination of pigments and the monitoring of colour alterations.

Zinc white and lithopone were chosen because they were extensively used since the end of the XVIII century; titanium white for its more recent artistic relevance, starting from the XX century.

Spectral reflection factors collected in the UV–visible range from suitable test models for each pigment highlight significant differences in the 350–450 nm range, as arisen from spectral manipulations. Peak locations and bandwidths were inferred from the first derivatives of the SRFs, so these parameters provided the markers for pigment discrimination and emphasized the distinct behaviours, in particular for zinc white. The results were about 384, 401 and 403 nm for peak wavelengths and about 9, 19 and 20 nm for bandwidths of zinc white, lithopone and titanium white, respectively.

The natural varnishes that commonly finish the artworks do not significantly alter the spectral shapes of the related samples, even if colour differences between varnished and unvarnished samples are not negligible.

Furthermore, to explore the possibility of supporting laser cleaning with colour measurements, every test sample was irradiated at increasing fluences by a pulsed excimer KrF laser and the colour damage thresholds were evaluated. In comparison with corresponding non-irradiated areas, it emerged that irradiation of samples at the CDT resulted in almost no modification of the SRF derivatives, despite the related colour distance.

CDT values of varnished samples were two or even three times larger than those of unvarnished samples. Significant colour shifts implied partial or full ablation of the varnishes, as also confirmed by SEM micrographs and EDX analyses.

Irradiation at the CDT fluence appeared to restore the original colour.

Future investigations will deal with the irradiation of artificially aged models covered with natural resins; the results will be compared with the data available in the literature [2, 16].

REFERENCES

1 M. Castillejo, M. Martín, M. Oujja, D. Silva, R. Torres, A. Manousaki, V. Zafiropulos, O.F. van der Brink, R.M.A. Heeren, R. Teule, A. Silva, H. Gouveia, Anal. Chem. **74**, 4662 (2002)
2 P. Bracco, G. Lanterna, M. Matteini, K. Nakahara, O. Sartiani, A. de Cruz, M.L. Wolbarsht, E. Adamkiewicz, M.P. Colombini, J. Cult. Herit. **4**, S202 (2003)
3 M. Castillejo, M. Martín, M. Oujja, J. Santamaría, D. Silva, R. Torres, A. Manousaki, V. Zafiropulos, O.F. van der Brink, R.M.A. Heeren, R. Teule, A. Silva, J. Cult. Herit. **4**, S257 (2003)
4 J. Hildenhagen, K. Dickmann, J. Cult. Herit. **4**, S174 (2003)
5 A. Sansonetti, M. Realini, J. Cult. Herit. **1**, S189 (2000)
6 P. Pouli, D.C. Emmony, C.E. Madden, I. Sutherland, J. Cult. Herit. **4**, S271 (2003)
7 M. Chappé, J. Hildenhagen, K. Dickmann, M. Bredol, J. Cult. Herit. **4**, S264 (2003)
8 M.I. Cooper, P.S. Fowles, C.C. Tang, Appl. Surf. Sci. **201**, 75 (2002)
9 R. Bordalo, P.J. Morais, H. Gouvela, C. Young, Laser Chem., DOI: 10.1155/2006/90279
10 M. Bacci, A. Casini, C. Cucci, M. Picolla, B. Radicati, M. Vervat, J. Cult. Herit. **4**, S329 (2003)
11 G. Dupuis, M. Elias, L. Simonot, Appl. Spectrosc. **56**, 1329 (2002)
12 R.W.G. Hunt, *Measuring Colour* (Fountain, London, 1998)
13 R.S. Berns, *Principles of Colour Technology* (Wiley, New York, 2000)
14 C. Oleari, *Misurare il coloure. Spettrofotometria, fotometria e colourimetria. Fisiologia e percezione* (Hoepli, Milano, 2002)
15 A. Schnell, L. Goretzki, C. Kaps, in *Proc. 8th Eur. Congr. Exhib. Advanced Materials and Processes (EUROMAT '03)*, Lausanne, Switzerland (2003)
16 C. Theodorakopoulos, V. Zafiropulos, C. Fotakis, J.J. Boon, J. v.d. Horst, K. Dickmann, D. Knapp, in *Proc. Lasers in the Conservation of Artworks (LACONA V)*, Osnabrück, Germany (2003), p. 255