INNOVATIVE METHODOLOGIES FOR THE ANALYSIS OF THE CONSERVATION STATE ON WOODEN SURFACES

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Colour variations on wood surfaces are due to photo-degradation of its chemical constituents, therefore the study of the relationship between colour changes and the chemical composition caused by irradiation is of practical and theoretical importance for the understanding of degradation phenomena. The Fourier transform infrared (FTIR) spectroscopy and reflectance spectrophotometry were used to assess artificial sunlight exposure. The statistical approach and the provisional and descriptive models obtained were the innovative results. Laser tests were carried out with the MDTT45 Q-switched Nd YAG changing the irradiation conditions in order to find the threshold values of fluence useful to remove the brownish surface layer on the investigated artefact. The examined species were lime, chestnut, poplar and beech. It was observed that wood colour shows high variability and the colour differences must be calculated on the same measurement point. Colour monitoring allowed to study the wood surface colour variation due to photo-irradiation. FTIR analysis highlighted that irradiation caused the degradation of lignin and increased concentration of the chromophore groups on the wood surface. FTIR spectroscopy allowed also to investigate the rate of photo-degradation of wood surface due to lignin oxidation.
The correlation between colour changes and lignin photo-degradation was determined in the species examined and qualitative and quantitative models have been developed. These results are very interesting because they demonstrate that colour measurements or reflectance spectro-photometry can be used to evaluate wood surface modifications in a totally non-destructive modality.

Keywords: wood colour, photo-degradation, fourier transform infrared (ftir) spectroscopy, reflectance spectrophotometry, laser cleaning.
Parole chiave: colore del legno, fotodegradazione, spettroscopia ftir, spettrofotometria in riflettanza, pulitura laser.

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1. Introduction

Colour variation of wood due to light radiation is an interesting and important topic in wood science as testified by a lot of literature papers concerning the photo-oxidation of wood surfaces (Agresti *et al*., 2013; Calienno *et al*., 2014; Calienno *et al*., 2015; Hon and Shiraishi, 2001; Lo Monaco *et al*., 2011; Pelosi *et al*., 2013a; Teacă *et al*., 2013; Tolvaj and Mitsui, 2010; Tolvaj *et al*., 2013). Colour variations on wood surfaces are due to photo-degradation of its chemical constituents, therefore the study of the relationship between colour and chemical changes caused by irradiation is of practical and theoretical importance for the understanding of degradation phenomena (Teacă *et al*., 2013).
The Fourier transform infrared (FTIR) spectroscopy and reflectance spectrophotometry were used to assess the effects of artificial sunlight on wood. The monitoring of wood surfaces exposed to radiations was performed by non-destructive methods to develop a methodology applicable also to the cultural heritage objects. The colour change is the most sensitive method to determine the extent of photo-degradation of wood exposed to ultraviolet and visible radiation. The obtained data were correlated to check the relationship between variation of colour and of the chemical components (Agresti *et al*., 2013; Calienno *et al*., 2014; Calienno *et al*., 2015; Pelosi *et al*., 2013a).

2. Materials and methods

The species investigated were poplar (*Popolus* sp.), beech (*Fagus sylvatica* L.), chestnut (*Castanea sativa* Mill.) and lime (*Tilia* sp.).
Colour was monitored by an X-Rite CA22 reflectance spectrophotometer. The characteristics were: colour scale CIEL*a*b*; illuminant D65; standard observer 10°;

geometry of measurement 45°/0°; spectral range 400-700 nm; spectral resolution 10 nm; measurement diameter 4 mm. The differences in lightness (ΔL*), in chromatic coordinates (Δa* e Δb*) and in total colour (ΔE*) were then calculated according to EN 15886 standard.

FTIR analysis was applied to study the chemical modifications of wood constituents caused by irradiation (Kataoka and Kiguchi, 2001; Moore and Owen, 2001; Pandey, 2005; Tolvaj *et al*., 2011; Agresti *et al*., 2013). FTIR spectra were obtained using a Nicolet Avatar 360 Fourier transform spectrometer, in diffuse reflection modality (DRIFT), with a resolution of 4 cm^{-1}. The relative changes in intensities of spectral bands associated with lignin and carbohydrates as a result of deterioration were determined at different exposure times.

Data were analyzed with the Statistica 2010 advanced statistics software. As a first step, data distribution was plotted and visually checked for normality. Differences among the samples were checked with ANOVA and M-ANOVA analysis. Post-hoc tests were conducted with Tukey HSD test method. Linear and non-linear regression analysis was used to develop prediction models (Agresti *et al*., 2013; Calienno *et al*., 2014; Calienno *et al*, 2015; Pelosi *et al*., 2013a).

Laser tests were carried out with the MDTT45 Q-switched Nd:YAG system supplied by MEDICAM, changing the irradiation conditions in order to find the threshold values of fluence useful to remove the brownish surface layer without damaging the wood support of the investigated artifact.

The experimental parameters were: wavelength 1064 nm and 532 nm, energy from 4 to 28 mJ, fluence from 0.01 Jcm^{-2} to 0.90 Jcm^{-2}, pulse duration 10 ns, spot diameter from 2 to 8 mm, frequency 5 Hz (Pelosi *et al*., 2013b).

3. Results

The wood of poplar, beech and chestnut undergoes chemical and colour changes due to light radiation in the solar box.

Colour monitoring on the examined species allowed to find that wood surface undergoes an important variation of colour due to photo-irradiation, occurring within the first 24 – 48 hours.

L* parameter clearly decreases. This can be attributed to photo-degradation processes mostly related to the decomposition of lignin due to the chromophore groups absorbing energy, especially in the UV range of the sunlight spectrum. The photo-degradation of the extractives can also affect the decrease of L* values.

The intensity of the FTIR bands associated with lignin decreases during photo-degradation.

This is accompanied by an increase in the intensity of the band associated to carbonyl absorption, as a function of irradiation time. This can be explained by the formation of C=O groups of degraded lignin. The intensities of the peak associated with carbohydrates is not significantly affected by irradiation.

3.1 Poplar

The important variation of colour on poplar wood surface exposed to photo-irradiation is mainly due to L* decrease and b* increase (Tab 1, 2 and 3) (Agresti *et al*., 2013; Pelosi *et al*., 2013a). FTIR spectroscopy allowed to investigate the rate of photo-degradation of wood surface due to lignin oxidation (Tab. 4). The most innovative result is that a correlation of the colour changes may be derived with the photo-degradation of lignin obtained by FTIR analysis (Tab. 5).

3.2 Beech

Colour monitoring on beech (Tab. 1, 2 and 3) (Calienno *et al*., 2014) highlighted a great variation of colour and Fourier Transform Infrared spectroscopy allowed to investigate the rate of photo-degradation of wood surface due to lignin oxidation (Tab. 4). The results of the regression analysis underlined that only the I_{1507}/I_{1375} peak ratio has a statically significant relation with the chromatic coordinates, in particular with L* and a* (Tab. 5).

3.3 Chestnut

Colour monitoring on chestnut (Calienno *et al*., 2015) showed that the important colour variation of wood surface due to photo-irradiation is mainly originated by L* decrease and b* increase (Tab. 1 and 2). FTIR analysis indicated that irradiation caused the degradation of lignin and increased the concentration of the chromophore groups on the wood surface (Tab. 4). Changes in the chromatic coordinates can be related to the degradation of lignin and to the increase of the concentration of carbonyl groups (Tab. 5).

3.4 Laser cleaning on lime

Laser cleaning tests were performed on a statue of lime wood (Fig. 1) (Pelosi *et al*., 2013b) under different conditions in order to find the threshold values of fluence that are useful to remove the brownish surface layer without damaging the wood support (A: 0.01 J/cm^2; B: 0.64 J/cm^2; C: 0.16 J/cm^2). The surface was analyzed before and after the cleaning, with the aid of a video microscope and a reflectance spectrophotometer. To evaluate the effectiveness in removing the brownish shellac layer, video microscope acquisitions and twelve points for colour measurements were chosen in the three tested area, before and after the laser irradiation. The laser tests allowed finding the suitable parameters making possible to remove almost completely the shellac layer without damaging the wood surface (B test). The effectiveness of the laser cleaning was explored by means of reflectance spectrophotometry, a simple method giving immediate and easy to understand data to evaluate the surface changes.

4. Conclusions

Wood colour shows high variability, for this reason data have to be collected from different areas of each sample to quantify and account for this variability and the colour differences must be performed on the same measurement

point. FTIR analysis highlighted that irradiation caused the degradation of lignin and increased concentration of the chromophore groups on the wood surface.
Colour monitoring allowed to find that wood surface colour undergoes an important variation due to photo-irradiation, occurring within the first 24-48 hours; FTIR spectroscopy allowed to investigate the rate of photo-degradation of wood surface due to lignin oxidation. The correlation between colour changes and lignin photo-degradation was determined in the species examined and qualitative and quantitative models have been developed. These results are very interesting because they demonstrate that colour measurements or reflectance spectrophotometry can be used to evaluate wood surface modifications in a totally non-destructive modality.
The laser cleaning applied to wood material can be an effective method to remove the surface deposits without affecting negatively the original support. The diagnostic analysis was fundamental to verify the applicability of the laser to the surface. Considering the reduced number of laser cleaning examples applied to wooden material available in literature, the documentation of the adopted working process could be a useful reference for the divulgation and sharing of the obtained data.

Table 1. L*, a* e b* chromatic coordinates at different times of exposure in Solar Box for Poplar, Beech and Chestnut.
Tabella 1. Coordinate cromatiche L*, a* e b* a differenti tempi di esposizione nel Solar Box per Pioppo, Faggio e Castagno.

	Poplar			*Beech*			*Chestnut*		
Time (h)	*L**	*a**	*b**	*L**	*a**	*b**	*L**	*a**	*b**
0	84.3	2.0	16.8	82.1	4.9	17.4	75.9	5.8	20.3
12	81.9	2.1	22.7	73.4	8.4	24.5	71.6	6.9	28.1
24	80.9	2.6	25.3	71.9	9.9	27.9	68.8	7.6	30.2
48	80.0	3.4	27.6	70.8	9.8	27.9	66.6	8.4	31.4
72	79.7	4.0	29.9	70.2	9.8	28.2	67.9	8.9	32.8
96	78.3	4.5	29.4	69.2	9.1	27.5	66.7	9.5	33.2
120	78.1	4.8	29.9	69.4	9.0	27.6	66.2	9.5	32.8
144	77.9	5.2	30.3	69.3	9.1	27.9	65.9	9.4	32.3
168	77.7	5.7	31.4	69.5	10.0	29.9	64.9	10.1	33.4
216	76.4	7.1	33.1	68.4	9.5	29.1	63.3	9.0	30.4
312	72.7	8.9	33.1	69.2	9.7	29.9	63.1	8.8	29.5
408	71.7	8.7	32.2	69.0	9.4	29.5	63.7	9.0	29.6
504	71.6	9.5	33.3	69.0	9.5	29.6	63.7	9.8	30.0

Table 2. Regression analysis for the dependent variables L*a*b* as function of the exposure time (t).
Tabella 2. Regressione per le variabili dipendenti L* a* b* in funzione del tempo di esposizione (t).

Poplar			
	Regression	*R^2adj.*	*Significance*
L*	$83.002-0.045t+0.00004t^2$	0.816	***
a*	$1.569+0.032t-0.00003t^2$	0.954	***
b*	$20.108+0.00679t-0.00008t^2$	0.857	***
Beech			
	Regression	*R^2adj.*	*Significance*
L*	$76.615-0.045t+0.00005t^2$	0.541	**
a*	$6.963+0.020-0.00002t^2$	0.489	**
b*	$22.19+0.053t-0.00006t^2$	0.684	**
Chestnut			
	Regression	*R^2adj.*	*Significance*
L*	$70.392-0.037t+0.00005t^2$	0.729	**
a*	$6.843+0.018t-0.00002t^2$	0.736	**
b*	$24.720+0.046t-0.00007t^2$	0.719	**

Table 3. Regression analysis for the dependent variable t (time) as function of the L*a*b* coordinates.
Tabella 3. Regressione per la variabile dipendente t (tempo) in funzione delle coordinate cromatiche L* a* b*.

Poplar
R^2adj.=0.947; $p<0.001$
$t=1732.3-56.2L^*+16.2a^*+24.5b^*+0.4L^{*2}+4.4a^{*2}-0.5b^{*2}$
Beech
R^2 adj.=0.891; $p<0.01$
$t=10525.09-256.27L^*+121.18a^*-111.61b^*+1.67L^{*2}-11.27^{*2}+3.03b^{*2}$

Table 4. Regression analysis for the dependent variable peak intensity ratio as function of the exposure times.
Tabella 4. Regressione per la variabile dipendente rapporto della intensità dei picchi in funzione del tempo di esposizione.

Poplar		
Function	*R^2adj.*	*Significance*
$I_{1507}/I_{1376}=1.383e^{-0.005t}$	0.865	***
$I_{1737}/I_{1376}=2.808+0.003t$	0.129	*
$I_{1507}/I_{1737}=0.995+0.0031t-0.109t^{0.5}0.109t0.5$	0.924	***
Beech		
Function	*R^2adj.*	*Significance*
$I_{1507}/I_{1375} = 1.431-0.006t+0.000007t^2$	0.777	**
$I_{1507}/I_{1375} = 1.45+0.004t$	0.412	**
$I_{1739}/I_{1507} = 1{,}26-0{,}004t+0{,}000004t^2$	0.613	**
Chestnut		
Function	*R^2adj.*	*Significance*
$I_{1507}/I_{1375} = 1.846+0.00096t-0.084t^{0,5}$	0.819	**
$I_{1507}/I_{1375} = 4.323-0.004t-0.192t^{0,5}$	0.224	**
$I_{1507}/I_{1739} = 0.415+0.00045t-0.026t^{0,5}$	0.938	**

Table 5. Regression analysis for the dependent variable peak intensity ratio as function of the chromatic coordinates.
Tabella 5. Regressione analysis per il rapporto della intensità dei picchi in funzione delle coordinate cromatiche L* a* b*.

Poplar
I_{1507}/I_{1376}
R^2adj.=0.999
$I_{1507}/I_{1376}=1.4582+0.000092L^{*2}-0.00373a^{*2}-0.001328b^{*2}$
I_{1507}/I_{1737}
R^2adj.=0.995
$I_{1507}/I_{1737}=-12.420+0.0017L^{*2}-0.0072a^{*2}+0.0032b^{*2}$
Beech
I_{1507}/I_{1376}
R^2adj.=0.892; $p<0.01$
$I_{1507}/I_{1375} = -21.948+2.953a^*+0.002L^{*2}-0.163a^{*2}$
Chestnut
I_{1507}/I_{1375}
R^2adj.=0.609; $p<0.01$
$I_{1507}/I_{1375}=-23{,}466+1{,}267L^*-1{,}636a^*-0{,}642b^*-0{,}0097L^{*2}+0{,}48402778a^{*2}+0{,}08680556b^{*2}$
I_{1507}/I_{1739}
R^2adj.=0.808; $p<0.01$
$I_{1507}/I_{1739} = -4{,}494+0{,}238L^*-0{,}393a^*-0{,}097b^*-0{,}00179L^{*2}+0{,}01794a^{*2}+0{,}0019b^{*2}$

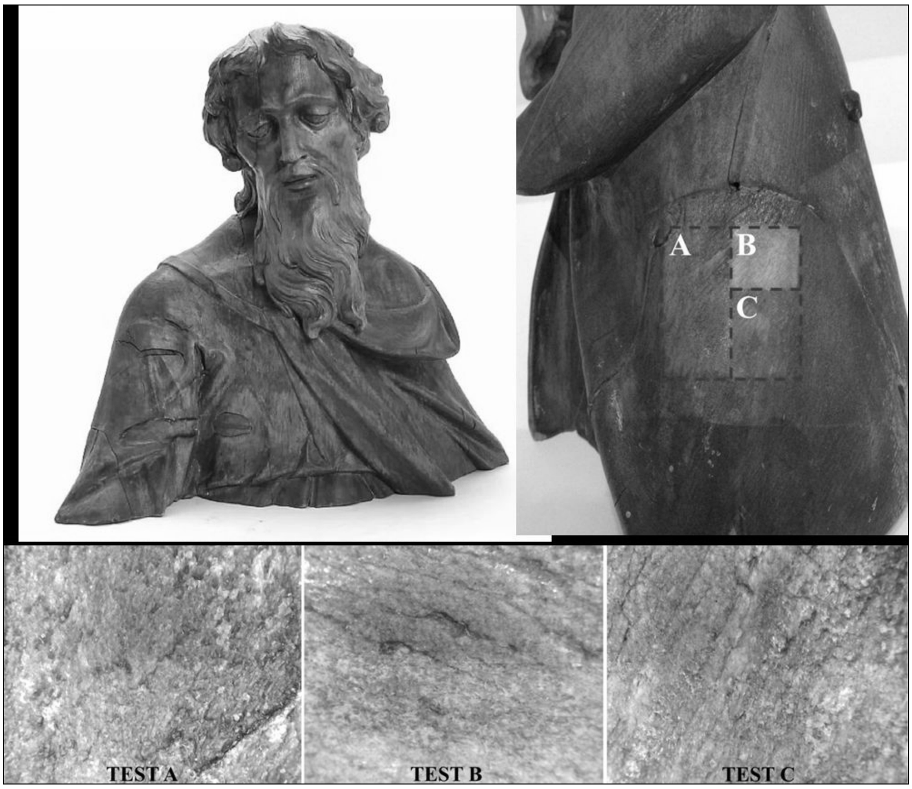

Figure 1. The sculpture representing Saint Joseph by the workshop of Ignaz Günther (1727-1775) carved on lime wood.
Figura 1. Scultura in legno di Tiglio rappresentante San Giuseppe, attribuita alla bottega di Ignaz Günther (1727-1775).

RIASSUNTO

Metodologie innovative per l'analisi dello stato di conservazione di superfici lignee

La variazione di colore è uno dei metodi più sensibili per svelare il grado di fotodegradazione del legno esposto a radiazione nell'ultravioletto e nel visibile, quindi lo studio del rapporto tra i cambiamenti di colore e della composizione chimica causata da irradiazione è d'importanza pratica e teorica per la comprensione dei fenomeni degradativi.
La spettroscopia infrarossa in trasformata di Fourier (FTIR) e la spettrofotometria in riflettanza sono state impiegate per valutare l'influenza della luce. Approccio statistico e modelli previsionali e descrittivi ottenuti costituiscono l'innovazione. Test con laser sono stati effettuati con un sistema Nd:YAG Q-switched, variando le condizioni di irraggiamento anche al fine di trovare i valori di soglia di fluenza utili alla rimozione dello strato superficiale brunastro sul manufatto studiato. Le specie esaminate sono tiglio, castagno, noce, pioppo e faggio.
È stato osservato che il colore mostra un'elevata variabilità e le differenze colorimetriche devono scrupolosamente essere verificate negli stessi punti. Il monitoraggio del colore ha permesso di verificare le variazioni di colore causate dalla foto-irradiazione. L'analisi FTIR ha evidenziato che l'irradiazione ha causato la degradazione della lignina aumentando la concentrazione dei gruppi cromofori sulla superficie del legno. La spettroscopia FTIR ha permesso di indagare il tasso di fotodegradazione della superficie del legno dovuto all'ossidazione della lignina. La correlazione tra cambiamenti di colore e fotodegradazione della lignina è stata determinata nelle specie esaminate e sono stati creati modelli qualitativi e quantitativi.
Questi risultati dimostrano che le misurazioni di colore, con la spettrofotometria di riflettanza, possono essere impiegate per valutare le modifiche superficiali del legno in modo totalmente non distruttivo.

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