

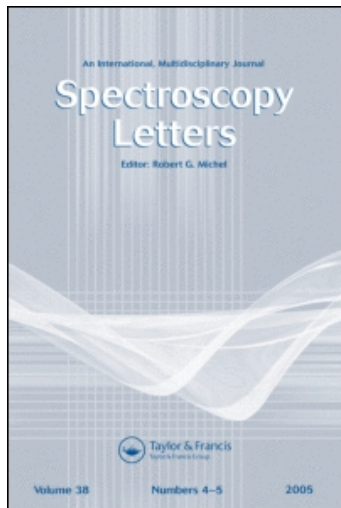
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An Investigation of the Reciprocity Principle of Light Exposures Using Microfading Spectrometry

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ABSTRACT It is frequently assumed that sensitive museum materials follow the reciprocity principle of light exposures. Thus, equivalent exposure doses obtained by using either high-illuminance levels for short periods of time or lower illumination for longer exhibition periods are believed to cause similar degrees of damage to an object. Microfading spectrometry permitted the investigation of this phenomenon by evaluation of light-induced changes in a series of samples. The effects of equivalent exposure doses on materials such as Blue Wool 1, LightCheck Ultra, and various dyed silks from a reference collection were compared. The results indicate that reciprocity is obeyed by the most stable colorants, while materials with lower stability to light may experience deviations that are proportional to the intensity of illumination. This study confirms that reciprocity failure is associated with the use of high-intensity lamps during accelerated-aging trials. Therefore only those tests conducted at low-illumination intensity ranges where reciprocity holds should be employed when one estimates the extent of damage occurring in a museum environment.

KEYWORDS microfading tester, photofading, reciprocity principle, visible reflectance spectroscopy

INTRODUCTION

The reciprocity law of light exposures was postulated in the mid-19th century by Bunsen and Roscoe.^[1,2] The method consisted of determining the amounts of chemical actions produced by direct and diffuse sunlight in photographic paper. The experiments were conducted using a pendulum photometer that provided an accurate way of measuring the times of exposure along strips of photographic paper of uniform sensitivity. The times recorded with the pendulum were correlated to the times obtained using light of various known intensities that produced different shades of tints on photographic paper. The experimental data demonstrated that equivalent light exposures that resulted in a comparable shade required intensities that were inversely proportional to the times of exposure. The law stated that different intensity-to-time ratios resulting in equal exposure

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doses produce the same photochemical effect on photographic paper and that therefore the two parameters are related by a constant c as expressed in the equation

$$I \times t = c,$$

where I is the intensity of the light source, and t is the time of exposure.

Deviations from the reciprocity law were later reported by a series of investigators towards the end of the 19th century. The first systematic studies on reciprocity failure were conducted by Schwarzschild in 1889 by evaluating photographic film sensitivity at long exposure times.^[3] When studying gelatin emulsion plates, Schwarzschild found that sources of light of different intensity I caused the same degree of blackening under different times of exposure t if the products of $I \times t^p$ were equal. Experimental evidence agreed with the theoretical model that consisted of raising the time of exposure t to the power of p , a constant value, instead of using the previous $I \times t$ equation proposed by Bunsen and Roscoe. However, further experiments demonstrated that p was constant only at narrow ranges of intensity, confirming that the photochemical properties of a material and the exposure dose ranges employed were the main factors accountable for these deviations. Further revisions of the reciprocity law resulted in new definitions such as those of *reciprocity principle* and *reciprocity concept*, which were later adopted.

More recently, several authors have investigated the reciprocity law in diverse areas such as biology, medicine, photography, polymer science, and conservation of cultural heritage.^[4–8] For example, some researchers have studied the sensitivity of museum materials to light using the reciprocity principle as a way of relating the exposure doses obtained from artificial aging to the ones typically encountered in a museum environment.^[9–12] Photometric measurements carried out in museums are sometimes extrapolated to annual light exposures based on the lighting schedules of each institution. Afterward, these annual exposures are used towards estimating the time required to reach a specific level of damage based on an equivalent exposure induced artificially. The color changes produced as a result of accelerated aging are assessed using spectroscopic and colorimetric methods. Light-fastness tests conducted on a

series of pigments and photographic papers typically found in museum collections revealed that the reciprocity principle is followed.^[8,13] However, further investigations in the photographic field have shown reciprocity failure when higher illumination intensities are employed for short periods of time and also when attempting to describe the photoresponse of a material as a function of radiant flux.^[14–16]

The high sensitivity to light exhibited by several organic dyes found in paintings and textiles has been a matter of concern to museum conservators and curators. These materials have high susceptibility to color alterations resulting from exposure to display lights making the establishment of adequate exhibition periods a very difficult task. It is also known that the fading of a colorant is a complicated process involving internal factors such as its chemical reactivity and physical state within the fabric together with external factors like exposure to oxygen and atmospheric pollutants.

Blue Wool (BW) standards have been extensively used as a reference scale when conducting artificial weathering tests on museum materials.^[17–19] BW standards have been in use since 1914, and were originally developed by the German Commission for Fastness (Deutsches Echtheits Kommission DEK).^[20] They consist of a reference set of blue-dyed wools attached to a white cardboard substrate. There are 8 standards each exhibiting increasing light-fastness by a factor of two, relative to the previous one, with BW 1 being the most light sensitive dye. Qualitative and quantitative determinations of the degree of fading can be made by examining the color changes produced as a result of exposure of BW standards to light.^[21] Fading of a BW standard can be followed visually by evaluating tonal changes of the blue dye as the exposure dose increases. As the reaction progresses, the more sensitive dyes become lighter while extreme exposure doses may result in total disappearance of color.

In recent years, LightCheck[®] Ultra (LCU) standards were developed in France due to the necessity of studying lower light exposure ranges than the ones covered by BW standards.^[22,23] LCU standards consist of a mixture of photosensitive dyes embedded in a polymer matrix and applied on a paper substrate. When the LCU standard is exposed to light, a gradual change in color from blue to pink proportional to the exposure dose is observed.

The standard is then compared to a visual scale that relates the final color with an equivalent luminous exposure in lux-hours ($\text{lx} \cdot \text{h}$). In the present study, the sensitivity of BW 1 and LCU standards has been evaluated and their responses to visible light of various intensities have been investigated with the aim of determining the intensity ranges where reciprocity is fulfilled.

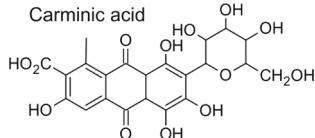
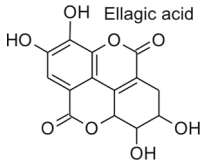
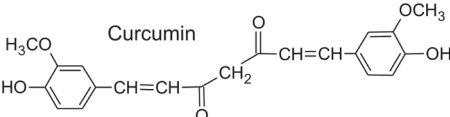
Furthermore, various silk samples dyed with natural colorants were also tested for reciprocity. These dyed silks belong to a reference set of samples prepared using materials and techniques similar to those found in 18th century Spanish textiles. The dyes investigated were cochineal, pomegranate and turmeric; their main coloring agents are: 7- α -D-glucopyranosyl-9,10-dihydro-3,5,6,8-tetrahydroxy-1-methyl-9,10-dioxanthracene carboxylic acid (carminic acid), 2,3,7,8-tetrahydroxy-chromeno[5,4,3-cde]chromene-5,10-dione (ellagic acid), and (1E,6E)-1,7-bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione (curcumin), respectively. Carminic acid is a glycoside which constitutes the coloring agent in carmine. It is typically found in some scale insects such as the cochineal and the Polish cochineal. The molecule consists of a core anthraquinone structure connected to a glucose sugar unit and it is known for its high light-fastness.^[24] The main coloring agent of pomegranate dye is ellagic acid which is found in the rind of the pomegranate fruit.^[25] This chromophore is characterized by a fused four-ring phenolic lactone compound. It has a planar structure that includes two lactone carbonyl groups that do not

deviate from the molecular plane. The chromophoric structure present in turmeric is curcumin which has two polyphenols connected by two α,β -unsaturated carbonyl groups. Curcumin is known for having very high sensitivity to oxygen and light.^[26] Molecular structures of the main chromophore present in each dye are presented in Table 1.

Several researchers have studied the stability of organic colorants applied on textile substrates and have classified them according to their light-fastness properties using the BW standards as a measuring scale.^[26–29] These testing programs have employed traditional accelerated-aging methods in which samples are exposed to high-intensity light sources inside weathering chambers at increasing time intervals. Reflection spectra and colorimetric parameters are recorded after each increment in light exposure providing an analytical way of evaluating the permanence of materials. Fewer investigations have employed real time techniques for evaluating the light-fastness of sensitive materials.^[21,30]

The aim of this work was to evaluate the use of a microfading tester (MFT) for determining approximations or deviations from the reciprocity principle using different equivalent exposure doses. Spectral and colorimetric information obtained using various intensities of illumination have permitted evaluating if equivalent exposure doses produce comparable changes in a particular sample. This study presents significant new information about a phenomenon that has not been investigated extensively although it is frequently mentioned in the museum science

TABLE 1 Summary of Main Coloring Agents Present in the Examined Dyes

Common name of dye	Part used to extract the dye	CI constituent	Main chromophore
Cochineal	Insect body	Natural red 4 CI 75470	 <p>Carminic acid</p>
Pomegranate	Rind of fruit	CI 75270	 <p>Ellagic acid</p>
Turmeric	Plant rhizome	Natural yellow 3 CI 75300	 <p>Curcumin</p>

literature. It is typically assumed that most materials in museum collections follow the reciprocity principle of light exposures. As a consequence, the information derived from traditional accelerated-aging trials is usually employed when estimating the degree of damage that a material will undergo if exposed to lower light levels for long periods of time. This research was conducted to allow researchers' making more-informed exhibition-lighting decisions that consider the chemical nature of a colorant and its physical state within the substrate, since approximation or deviation from reciprocity mainly depends on these two aspects. Traditional accelerated-aging methods involve performing subsequent spectroscopic measurements of each sample after every aging cycle. The constant movement of the sample between readings and the difficulties associated with measuring the exact same spot every time tend to increase the amount of error in these determinations. For this reason, it was believed that a real time technique such as the MFT would permit investigating and comparing fading rates of materials using various intensities in a more efficient way. Although microfading spectrometry results agree well with published light-fastness data acquired using traditional methods,^[26–28] the MFT offers a more accurate way of performing light-stability tests on materials since the exact same spot is measured over a relatively short period of time.

MATERIALS AND METHODS

Materials

BW and LCU standards were purchased from Talas (New York, NY) and Keepsafe Microclimate Systems (Toronto, Canada), respectively. Both materials were used as received. Dyed silk samples were kindly provided by Antonio Fernando Batista-dos Santos. Three dyes from this group of samples were considered for the present study: cochineal, pomegranate, and turmeric. Turmeric and cochineal dyes were obtained from Kremer Pigments, Inc. (New York, NY), while pomegranate dye was obtained from a local supplier in Valencia, Spain. Two silk samples were treated with $KAl(SO_4)_2$ mordant and dyed with cochineal and pomegranate, resulting in red and pale yellow samples, respectively. Turmeric was applied as a direct dye giving an intense yellow color to the silk. The preparation of the dyes and dyeing methods are described elsewhere.^[31]

Instrumentation

The MFT used in this study was developed by Whitmore and coworkers from the Art Conservation Research Center at Carnegie Mellon University in Pittsburgh.^[32] Individual components of this instrument are manufactured by Newport Oriel Corporation (California, U.S.A.) and are sold as Oriel 80190 Fading Test System (Stratford, CT). The device consists of a visible reflectance spectrophotometer coupled to an accelerated light fading microtester. The sensitivity of objects to high-intensity visible light can be determined by using short increments in exposure time to a 75-watt xenon arc-light source. Spectrocolorimetric data are recorded periodically and their change is evaluated over time. The instrument uses a 0/45 geometry for illumination of the sample and collection of reflected light. The diameter of the illuminated spot is approximately 0.4 mm and the working distance measured from the external lens of the illuminating probe to the surface of the sample is approximately 1 cm. The tests are conducted in open-air under laboratory room conditions ($T = 25^\circ\text{C} \pm 1$; $RH = 50\% \pm 1$). The intensity of the illuminated spot was reduced by inserting a series of 16 mesh aluminum wire circles of 51 mm of diameter in the multiple filter holder part of the instrument. The intensity of the illuminated spot was measured with an ILT 1700 radiometer from International Light Technologies (Peabody, MA) using a probe calibrated for point sources. Illumination intensities used were in the range of 0.1–4.0 Megalux (Mlx). The integration time used was 6 ms and 10 spectra were averaged. The Commission Internationale de l'Eclairage (CIE) illuminant and observer combination used was D_{65} and 2° , respectively.

Calculations

Reflectance spectra contain all the information required to evaluate the color of a sample during a microfading test. However, spectral data was reduced to a set of parameters according to existing conventions adopted by the CIE for describing color.^[33] These conversions permit researchers to evaluate complex color changes, which usually involve shifts in hue and lightness. Hence color differences were calculated using the CIE $L^*a^*b^*$ equation. This formula is widely employed in the conservation science field since most museum curators and

conservators are interested in assessing color changes that are perceptible to the human eye. The values in the CIE 1976 color space are L^* , a^* , and b^* used to designate lightness–darkness, redness–greenness, and yellowness–blueness, respectively. CIE $L^*a^*b^*$ values are calculated from measured tristimulus $X Y Z$ values and the corresponding $X_n Y_n Z_n$ values of the standard illuminant and observer combination used. Reflectance spectra of each test spot were collected and color differences were calculated using the initial spectrum as the basis for comparison. For example, the difference between two color measurements recorded at times t_1 and t_2 ($t_2 > t_1$) is given by:

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

where ΔE^* is the total change in color which depends on the three color parameters explained above. The CIE $L^*a^*b^*$ color difference equation provides a mathematical way of relating spectrophotometric changes to the ones perceived by a human observer. However, some discrepancies in ΔE^* values regarding a just noticeable difference (JND), which may range from 1 to 3, have been observed.^[34–36] Nevertheless, a ΔE^* of 5 has been considered large enough to be detected by most observers^[37] and has been used as an initial threshold value in the present study. If necessary, a lower ΔE^* value was selected as a stopping point since some materials exhibited higher stability to light making it difficult to produce a ΔE^* of 5 within a reasonable time of exposure. Microfading curves were adjusted for the exposure dose by multiplying the times of exposure by the intensity of illumination. If the reciprocity principle is followed, adjusted ΔE^* versus exposure dose curves are expected to show similar trends. Furthermore, the logarithms of the exposure doses (lx · h) required to induce a determined color change were calculated and their variation with the illumination intensity employed was also investigated.

RESULTS AND DISCUSSION

Changes in the reflectance spectrum of a BW 1 standard at various stages of a microfading test carried out using an intensity of 4 Mlx are presented in Fig. 1. The BW 1 reflectance spectrum is characterized by a broad band with a maximum around 440 nm and part of a larger band observed in the 650–700-nm region.

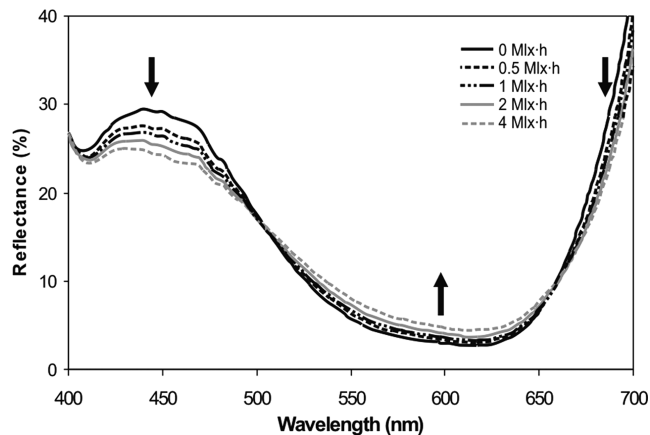


FIGURE 1 Evolution of visible reflectance spectra of a BW 1 standard obtained using an illumination intensity of 4 Mlx. The arrows indicate the direction of the spectral changes.

The fading of BW 1 is characterized by a loss of blue colorant evidenced by a reduction of the reflectance band in the 410–500-nm region as the light exposure increases. Simultaneously a decrease in reflectance is observed in the 660–700-nm portion of the spectrum accompanied by increasing reflections in the 500–650-nm region. Superposition of reflectance spectra shows isosbestic point behavior at 505 nm and 650 nm.

Figure 2 shows the times required to reach ΔE^* values of 2, 3.5, and 5 for a BW 1 standard using various illumination intensities in the 0.25–4-Mlx range. An asymptotic behavior can be observed at both ends of these curves. At higher intensities, ΔE^* values are reached rapidly and the times required to arrive at the stopping point become very similar. On the contrary, at lower illumination intensities the data shows higher dispersion and different final ΔE^* values become evident. Exposure doses required to

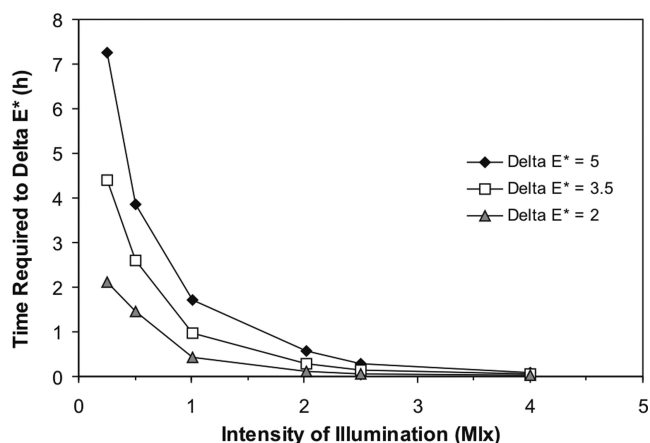


FIGURE 2 Times required to reach specific ΔE^* stopping points for a BW 1 standard at various illumination intensities.

TABLE 2 Exposure Doses Required to Induce a $5\Delta E^*$ Change in BW 1 and LCU Standards

Illumination intensity (Mlx)	Exposure dose for BW 1 (Mlx · h)	Exposure dose for LCU (Mlx · h)
0.25	1.8	0.13
0.5	1.9	0.15
1.0	1.7	0.058
2.0	1.2	0.042
2.5	0.7	0.046
4.0	0.4	0.033

induce a $5\Delta E^*$ color change for BW 1 and LCU standards are reported in Table 2.

Microfading curves obtained for a BW 1 standard using various combinations of illumination intensity and time of exposure are shown in Fig. 3a. Very rapid color changes were observed in the 2–4-Mlx intensity range while more gradual variations were observed at lower intensities. As the light intensity was reduced,

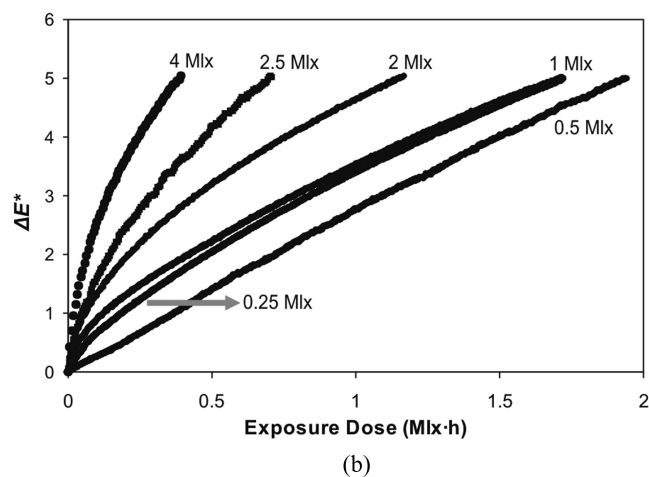
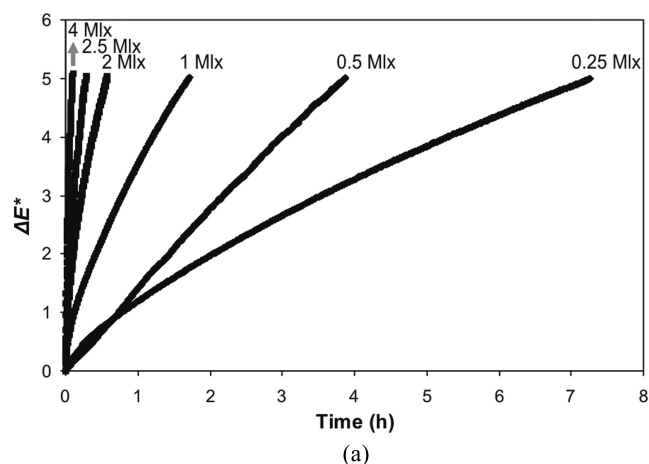


FIGURE 3 Micro-fading curves obtained for a BW 1 standard using various illumination intensities (a) the same fading data normalized for exposure dose in Mlx · h (b).

a longer exposure was necessary to reach the $5\Delta E^*$ stopping point. Microfading curves of BW 1 were adjusted for the exposure dose and the results are presented in Fig. 3b. It can be seen that fading rate decreases as exposure dose increases. Microfading curves adjusted for the exposure dose exhibit Type II fading behavior for the three higher illumination intensities while areas tested at lower power exhibit constant or type III fading. This description is based on five types of fading rate curves originally described by Giles.^[38] If reciprocity held all the curves would show similar trends. However, the plots start becoming similar only at lower intensities that range from 1 to 0.25 Mlx. After normalizing for exposure dose, microfading curves for 1 and 0.25 Mlx are very similar while the one obtained for 0.5 Mlx shows some deviation. Initially, this may suggest that the area measured using an intensity of 0.5 Mlx had a slower fading rate resulting in a non-linear response in the power range below 1 Mlx. However, after inspecting the original fading curves (Fig. 3a) it can be observed that this is just a consequence of the adjustment for the exposure dose. Moreover, fading behaviors observed at lower intensities are almost linear with increasing exposure dose and confirm that reciprocity is obeyed in this illumination range.

Figure 4 shows the evolution of reflectance spectrum with increasing light dose observed for a LCU standard. The visible reflectance spectrum of the LCU standard is characterized by a band in the 400–520-nm region with maximum at 422 nm and a shoulder around 508 nm. The spectrum also shows a reflection band in the 535–600-nm region with a

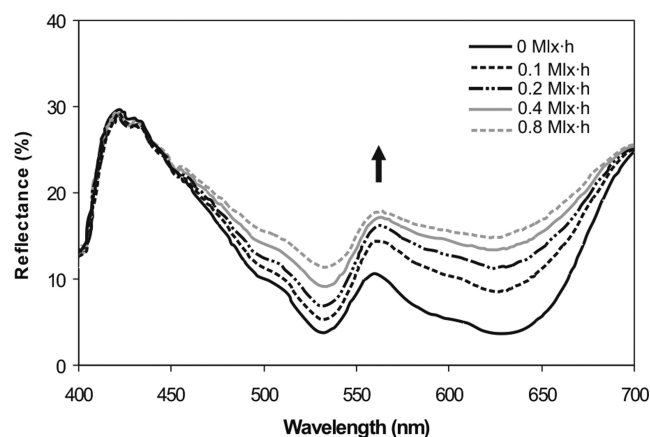


FIGURE 4 Evolution of visible reflectance spectra of a LCU standard obtained using an illumination intensity of 4 Mlx. The arrow indicates the direction of the spectral changes.

maximum around 560 nm. A portion of a third band is also observed from 630 to 700 nm. As the microfading test proceeds, the band in the blue region of the spectrum remains almost unchanged with the exception of increased reflectance observed in the 455–520-nm region indicating that the sample becomes lighter and greener with time. This effect is confirmed by an increase in reflectance of the band in the green portion of the spectrum, which was accompanied by a 4-nm hue shift towards the red. An increase in reflectance of the band in the 630–700-nm region was also observed during accelerated light aging. This data is consistent with reported changes for LCU standards consisting of increasing lightness and redness with higher exposure to light.^[23]

LCU standards showed different fading trends to the ones exhibited by BW 1. Microfading test results obtained for a LCU standard using six different illumination intensities are shown in Fig. 5a. Very rapid increases were observed when operating in the 1–4-Mlx illumination intensity range. In contrast, a more gradual increase in ΔE^* was observed as the intensity was reduced from 1 to 0.5 Mlx. The higher sensitivity of LCU standards relative to BW 1 becomes apparent after inspecting the times of exposure required to produce similar color changes on both materials. This higher sensitivity of LCU relative to BW 1 has been described by other authors.^[22,23] Microfading curves of the LCU standard adjusted for the exposure dose are presented in Fig. 5b. On the higher intensity end, microfading curves obtained using 2 and 2.5 Mlx are almost identical suggesting that a 0.5 Mlx difference in that intensity range results in comparable fading rates. Similar fading curves are also observed in the lower energy range indicating that LCU standards follow the reciprocity principle at illumination intensities which are below 0.5 Mlx.

The \log_{10} of the exposure dose required to reach a ΔE^* of 5.0 was calculated for both BW 1 and LCU standards and it was plotted against intensity of illumination (Fig. 6). Average \log_{10} exposure dose values were obtained for each standard in the range where reciprocity is observed and are indicated by horizontal discontinuous lines. From these plots, it can also be observed that BW 1 is more stable to light relative to LCU since the latter one required lower exposure doses to reach the $5\Delta E^*$ threshold value

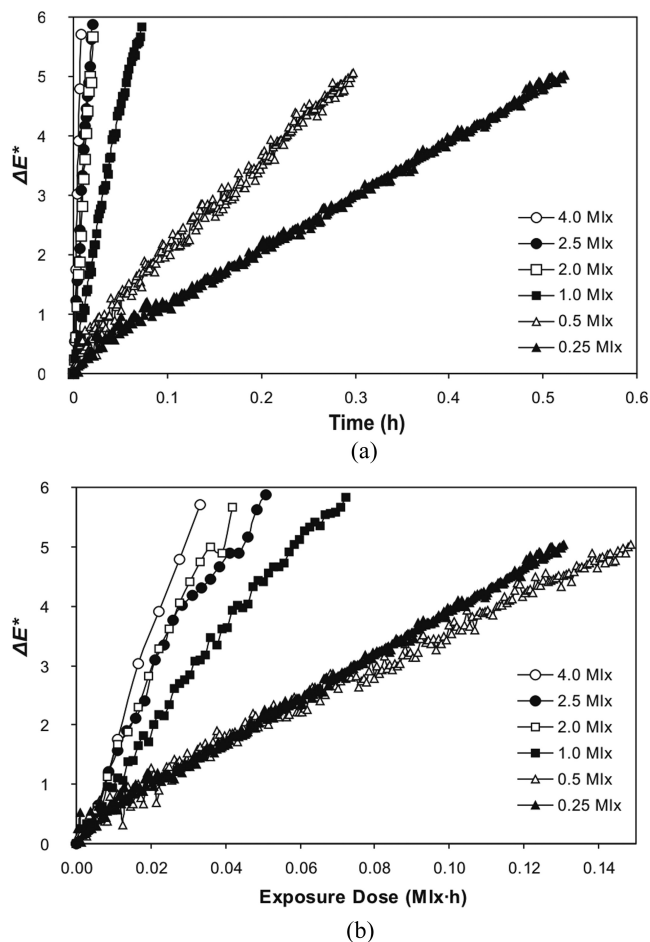


FIGURE 5 Micro-fading curves obtained for a LCU standard using various illumination intensities (a) the same fading data normalized for exposure dose in Mlx·h (b).

at all intensities. This higher stability of BW 1 is also apparent from the larger illumination intensity range where reciprocity holds (0.25–1 Mlx) relative to LCU

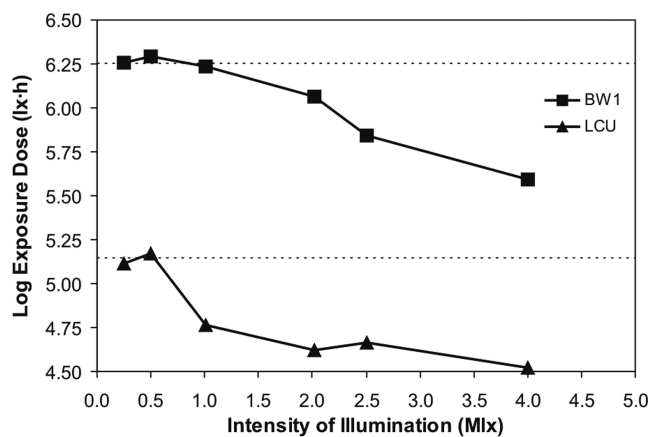


FIGURE 6 \log_{10} of exposure dose required to reach a ΔE^* of 5 versus intensity of illumination obtained for BW 1 and LCU standards. Discontinuous lines indicate average values calculated for lower intensities where reciprocity is observed.

(0.25–0.5 Mlx). These results indicate that illumination intensity intervals where reciprocity is obeyed must be employed when performing microfading tests on materials which have comparable light-sensitivity to any of these two standards. Otherwise, the material may fade in an unnatural way due to severe illumination intensities.

Figure 7 shows initial and final reflectance spectra obtained for three different silk samples dyed with cochineal, pomegranate, and turmeric. These samples were exposed to a 2 Mlx·h exposure dose obtained using an illumination intensity of 4 Mlx. The sample dyed with turmeric absorbs light in the 400–475-nm region of the visible spectrum resulting in a reflectance spectrum characterized by a broad band in the 500–700-nm wavelength range. As a result of accelerated light aging, the turmeric/silk system experiences a reduction in greenness evidenced by a 2% decrease in reflectance observed in the 550-nm region. This change was accompanied by an increase of about 4% in reflectance in the violet-blue region of the spectrum. Initial and final reflectance spectra recorded for the turmeric/silk system show isosbestic behavior at 522 nm. This was verified by comparing spectra recorded at intermediate exposure doses such as 0.5 and 1 Mlx·h demonstrating that the stoichiometry of the reaction remains unchanged during the fading test and no secondary reactions occur during the considered time range. The reflectance spectrum of the silk dyed with pomegranate is characterized by a broad band in the 450–700-nm region. After a 2 Mlx·h exposure dose, this sample experienced an overall 5% reduction

in reflectance in the 500–700 nm wavelength range. After comparing initial and final reflectance spectra of the sample containing pomegranate dye, it can be observed that this colorant experiences increases in lightness and redness as a result of exposure to light. Cochineal is the most stable dye evidenced by minor changes in the reflectance spectrum detected after the microfading test. The spectrum of cochineal shows a reflection band in the 600–700-nm region with a maximum at 689 nm along with reflections of lesser intensity in the violet-blue portion. In this example, the final spectrum shows a slight reduction of the main reflectance band accompanied by a 3 nm shift of the peak maximum to higher wavelength.

Microfading curves adjusted for the exposure dose of three different silk samples dyed with turmeric, pomegranate, and cochineal are shown in Fig. 8. Fading tests were conducted at various illumination intensities ranging from 0.1 to 4 Mlx. Turmeric exhibited higher light-sensitivity with exposure doses of 0.2 and 0.9 Mlx·h required to induce a $5.0\Delta E^*$ color change at illumination intensities of 4 and 0.1 Mlx, respectively. Microfading curves of turmeric showing similarities between the 1 and 2 Mlx illumination intensities and also between the 0.1 and 0.5 Mlx data are presented in Fig. 8a. The data recorded using a 4 Mlx illumination intensity shows a faster initial fading rate followed by slower changes in ΔE^* after an approximate exposure dose of 1 Mlx·h is reached. The remaining microfading curves obtained for turmeric show a more linear trend in color change with increasing exposure dose relative to the trial conducted at the highest intensity. Microfading curves of pomegranate dye adjusted for the exposure dose are shown in Fig. 8b. A more rapid increase in ΔE^* was observed at the beginning of the test followed by slower changes in color after an exposure dose of about 0.75 Mlx·h was reached. Pomegranate has greater stability than turmeric demonstrated by a larger exposure of 0.7 Mlx·h required to reach a ΔE^* of 5.0 when operating at 4 Mlx. After a 2 Mlx·h exposure dose, the pomegranate sample shows a 3.1 difference in absolute ΔE^* values after comparing the 4 and 0.1 Mlx data. Turmeric on the contrary shows a 16.2 difference in absolute ΔE^* s obtained with the highest and lowest illumination intensities after the same exposure dose is reached. Although the pomegranate sample showed different fading rates at various intensities, microfading curves

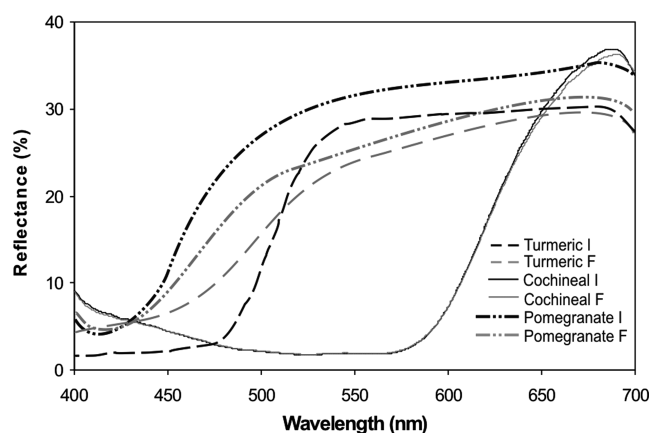


FIGURE 7 Comparison of initial (I) and final (F) reflectance spectra of curcumin, pomegranate, and cochineal after a 2 Mlx·h exposure dose obtained using an illumination intensity of 4 Mlx.

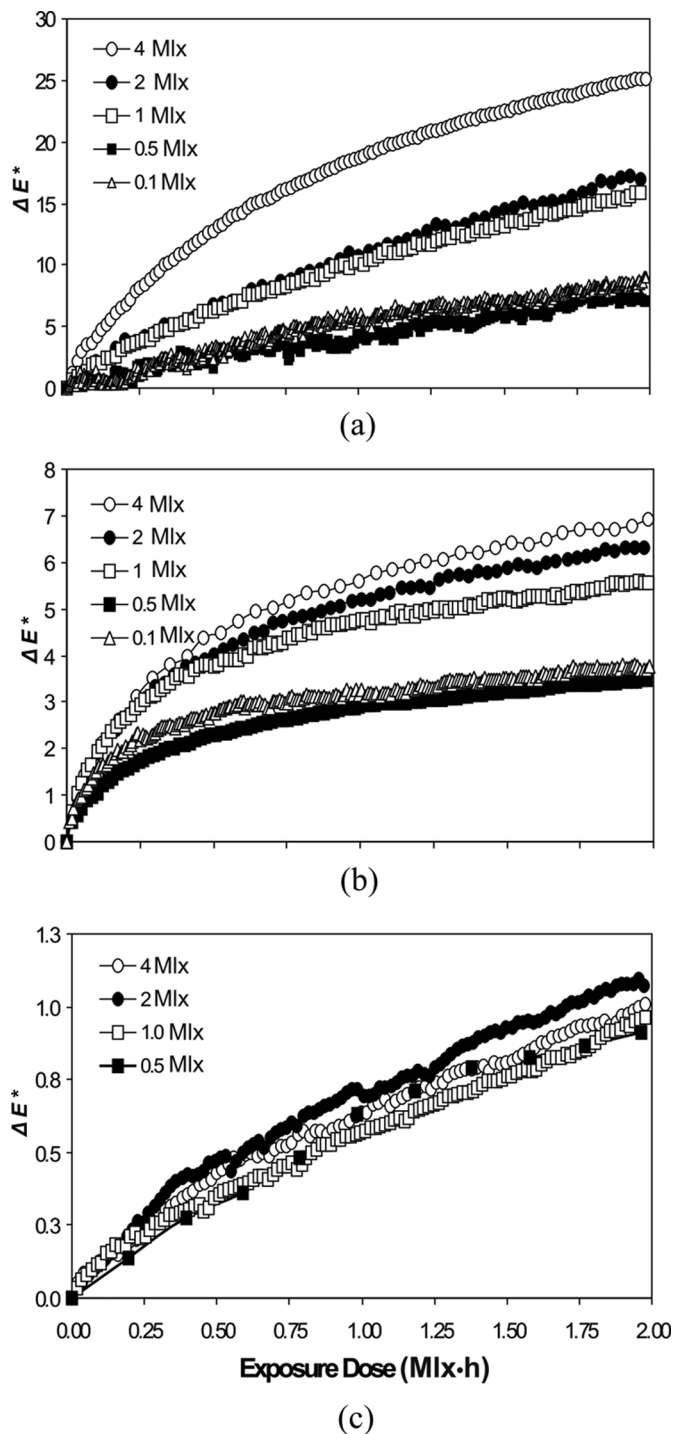


FIGURE 8 Micro-fading curves adjusted for exposure dose obtained for three different silk samples dyed with turmeric (a) pomegranate (b), and cochineal (c).

recorded at 0.1 and 0.5 Mlx were similar (Fig. 8b). As observed in Fig. 8c, cochineal is the most light-stable dye exhibiting its highest ΔE^* at 1.1 after a 2 Mlx·h exposure dose registered when using an illumination intensity of 2 Mlx. All microfading curves obtained for cochineal exhibited an almost linear relationship

TABLE 3 Exposure Doses Required to Induce 5, 3.5, and 1 ΔE^* Changes in Three Different Silk Samples Dyed With Turmeric, Pomegranate, and Cochineal, Respectively

Illumination intensity (Mlx)	Exposure dose for turmeric (Mlx·h)	Exposure dose for pomegranate (Mlx·h)	Exposure dose for cochineal (Mlx·h)
0.1	0.89	1.5	–
0.5	1.2	2.1	2.2
1.0	0.37	0.39	2.0
2.0	0.34	0.37	1.7
4.0	0.21	0.29	1.9

between color change and exposure dose. Table 3 presents the total light doses required to induce color changes with ΔE^* values of 5, 3.5, and 1 for turmeric, pomegranate, and cochineal, respectively. While color changes observed for turmeric and pomegranate are considered perceptible by human observers, total changes experienced by the cochineal sample would not be perceptible since they were approximately equal to 1.0 ΔE^* .

Figure 9 shows \log_{10} of exposure dose (lx·h) against illumination intensity for the three dyed silk samples evaluated. The relative stability to light of each sample is evident from the plot starting with cochineal as the most stable dye followed by pomegranate and then turmeric, which exhibited greater sensitivity. These results are consistent with published data on the light-stability of these dyes.^[26–28] The smaller deviations observed for cochineal in Fig. 8c are also evident in the \log_{10} exposure versus

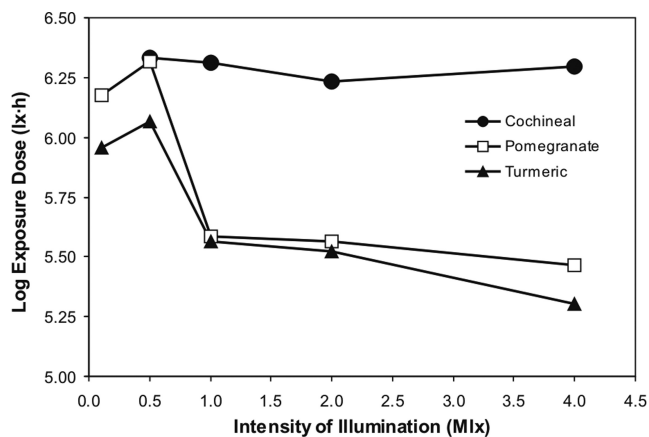


FIGURE 9 \log_{10} of exposure dose required to reach ΔE^* 's of 5, 3.5, and 1 versus intensity of illumination obtained for three different silk samples dyed with turmeric, pomegranate and cochineal, respectively.

illumination intensity plot. At the four illumination intensities studied, cochineal required similar exposure doses to reach a $1\Delta E^*$ endpoint. The plot of \log_{10} of exposure dose versus intensity also permits to distinguish two different stability levels for pomegranate and turmeric dyes.

Although external factors such as intensity of illumination, spectral distribution of the light source, temperature, relative humidity, and atmospheric pollution can affect the fading rate, it should be emphasized that the physical state of the colorant within the fiber has the largest influence on its light-fastness.^[39–41] Therefore, the fading rates of cochineal suggest that the dye is present in large aggregates within the silk since this physical state is known to improve light-fastness.^[26] It was observed that cochineal follows the reciprocity principle since adjusted microfading curves are almost identical. Moreover, anthraquinones are known for their low sensitivity to light.^[24,26] Pomegranate exhibited moderate sensitivity to light demonstrated by smaller changes in color at all illumination intensities relative to turmeric. Pomegranate also showed less dispersion of absolute final ΔE^* s relative to turmeric after comparing adjusted micro-fading curves obtained for both dyes. Zahri et al. have described the photo-degradation processes of various components of pomegranate dye such as ellagic acid and gallic acid.^[42] Turmeric was the least stable dye and its poor light-fastness is related to both its chemical structure and physical state. Although the ketoalkene part of the curcumin molecule provides a reaction center in which light can interact, the physical state of the colorant is more important in determining its low-light-fastness properties. As indicated by Cox-Crews, it is probable that turmeric does not form large aggregates within the fiber making the dye accessible to the action of light.^[26] Several photoproducts of curcumin along with their photodegradation mechanisms have been described by Sundaryono and coworkers.^[43]

Initial assessment of microfading curves obtained for a silk sample dyed with turmeric could wrongly indicate that reciprocity is true at illumination intensities below 2 Mlx. However, further tests conducted at lower intensities confirmed the presence of a different level of dye stability for which reciprocity is also followed in the 0.1–0.5-Mlx range. The same effect was observed for silk specimens dyed with pom-

egranate confirming the importance of performing microfading tests at the lowest possible illumination intensities. Although at initial glance the \log_{10} of exposure dose versus illumination intensity data obtained for pomegranate and turmeric looks similar, one must remember that the exposure doses evaluated are based on 3.5 and $5\Delta E^*$ endpoints, respectively.

CONCLUSIONS

This work constitutes the first feasibility study on the use of a MFT to conduct verifications of the reciprocity principle using materials found in museum collections. Microfading tests conducted at various illumination intensities, further adjustment of the fading curves for exposure dose, and plots of \log_{10} of exposure dose versus illumination intensities required to reach user-defined ΔE^* threshold values have demonstrated to be essential tools for reciprocity investigations. The results have shown that the reciprocity law postulated by Bunsen and Roscoe, originally established for simple photochemical reactions, cannot be merely transferred to the study of colored museum materials. Careful judgment should be exercised when establishing lighting parameters for museum exhibits which are based on accelerated light aging data since the reciprocity principle of light exposures generally holds only for the most stable artifacts while deviations should be expected for materials with high light-sensitivity. While the MFT provides a way of comparing the fading rates of several colorants, complementary analytical techniques may be employed to identify the chemical process of product degradations.

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REFERENCES

1. Bunsen, R. W.; Roscoe, H. E. Photo-chemical researches. Part IV. *Philos. Trans. R. Soc. Lond.* **1859**, *149*, 879–926.

2. Roscoe, H. E. The Bakerian Lecture: On a method of meteorological registration of the chemical action of total daylight. *Philos. Trans. R. Soc. Lond.* **1865**, *155*, 605–631.
3. Schwarzschild, K. On the deviations from the law of reciprocity for bromide of silver gelatine. *Astrophys. J.* **1990**, *11*, 89–91.
4. Marangoni, R.; Messina, N.; Gioffre, D.; Colombetti, G. Effects of UV-B irradiation on a marine microecosystem. *Photochem. Photobiol.* **2004**, *80*, 78–83.
5. Feng, L.; Suh, B. I. Exposure reciprocity law in photopolymerization of multifunctional acrylates and methacrylates. *Macromol. Chem. Phys.* **2007**, *208*, 295–306.
6. Merwald, H.; Klosner, G.; Kokesh, C.; der-Petrossian, M.; Hönigsmann, H.; Trautinger, F. UVA-induced oxidative damage and cytotoxicity depend on the mode of exposure. *J. Photochem. Photobiol. B* **2005**, *79*, 197–207.
7. Mamgain, S. P. Exposure and its effects, reciprocity law failure and hypersensitizing. *J. Ind. Soc. Rem. Sens.* **1981**, *9*, 21–28.
8. Saunders, D.; Kirby, J. Light-induced damage: Investigating the reciprocity principle. In *Proceedings of ICOM Committee for Conservation 11th Triennial Meeting, Edinburgh, Scotland, Sept. 1–6 1996*; Bridgland, J., Ed.; James and James: London, 1996; 87–90.
9. Feller, R. L. Control of deteriorating effects of light upon museum objects. *Museum* **1964**, *17*, 57–98.
10. Saunders, D.; Kirby, J. Light-induced colour changes in red and yellow lake pigments. *Nat. Gall. Tech. Bull.* **1994**, *15*, 79–97.
11. Duff, D. G.; Sinclair, R. S.; Stirling, D. Light-induced colour changes of natural dyes. *Stud. Conserv.* **1977**, *22*, 161–169.
12. Yatagai, M.; Magoshi, Y.; Becker, M. A.; Sano, C.; Ikuno, H.; Kohara, N.; Saito, M. Degradation and color fading of silk fabrics dyed with natural dyes and mordants. In *Historic Textiles, Papers, and Polymers in Museums*; Cardamone, J. M., Baker, M. T., Eds.; American Chemical Society: Washington, DC, 2001; 86–97.
13. Connors-Rowe, S. A.; Whitmore, P. M.; Morris, H. R. Optical brighteners in black-and-white photographic papers: Appearance and degradation. *J. Am. Inst. Conserv.* **2007**, *46*, 199–213.
14. Lavédrine, B. *A Guide to the Preventive Conservation of Photographic Collections*; The Getty Conservation Institute: Los Angeles, United States, 2003; pp. 304.
15. Holiday, E. R. Photographic methods. In *Analytical Absorption Spectroscopy, Absorptimetry and Colorimetry*; Mellon, M. G., Ed.; John Wiley and Sons: New York, 1950; 268–305.
16. Martin, J. W.; Chin, J. W.; Nguyen, T. Reciprocity law experiments in polymeric photodegradation: A critical review. *Prog. Org. Coat.* **2003**, *47*, 292–311.
17. Bullock, L.; Saunders, D. Measurement of cumulative exposure using Blue Wool standards. In *Proceedings of ICOM Committee for Conservation 12th Triennial Meeting, Lyon, France, Aug. 29-Sept. 3, 1999*; Brigland, J., Ed.; James and James: London, 1999; 21–26.
18. Michalski, S. Damage to museum objects by visible radiation (light) and ultraviolet radiation (UV). In *Lighting in Museums, Galleries, and Historic Houses, Papers of the Conference, Bristol, United Kingdom, Apr. 9–10, 1987*; The Museums Association: London, **1987**, 3–16.
19. Feller, R. L.; Johnston-Feller, R. The International Standards Organization's blue-wool fading standards (ISO R105). In *Textiles and Museum Lighting, Harpers Ferry Regional Textile Group Symposium, Washington, DC, United States, Dec. 4–5, 1980*; Harper's Ferry Regional Textile Group: Washington, DC, 1985; 41–57.
20. Wagner, R. S. D. Blue wool standards: standard reference fabrics for automotive lightfastness test methods. *Text. Chem. Color* **1987**, *19*, 27–31.
21. Bacci, M.; Cucci, C.; Mencaglia, A. A.; Mignani, A. G.; Porcinai, S. Calibration and use of photosensitive materials for light monitoring in museums, blue wool standard 1 as a case study. *Stud. Conserv.* **2004**, *49*, 85–98.
22. Laurence-Dupont, A.; Cucci, C.; Loisel, C.; Bacci, M.; Lavédrine, B. Development of LightCheck[®] Ultra, a novel dosimeter for monitoring lighting conditions of highly photosensitive artifacts in museums. *Stud. Conserv.* **2008**, *53*, 49–72.
23. Bacci, M.; Cucci, C.; Dupont, A. L.; Lavédrine, B.; Picollo, M.; Porcinai, S. Disposable indicators for monitoring lighting conditions in museums. *Environ. Sci. Technol.* **2003**, *37*(24), 5687–5694.
24. Timar-Balázsy, A.; Eastop, D. *Chemical Principles of Textile Conservation*; Butterworth-Heinemann: Oxford, United Kingdom, 1998; pp. 480.
25. Montazer, M.; Parvinzadeh, M.; Kiumarsi, A. Colorimetric properties of wool dyed with natural dyes after treatment with ammonia. *Color. Technol.* **2004**, *120*, 161–166.
26. Cox-Crews, P. The fading rates of some natural dyes. *Stud. Conserv.* **1987**, *32*, 65–72.
27. Padfield, T.; Landi, S. The light-fastness of the natural dyes. *Stud. Conserv.* **1966**, *11*, 181–196.
28. Yoshizumi, K.; Cox-Crews, P. Characteristics of fading of wool cloth dyed with selected natural dyestuffs on the basis of solar radiant energy. *Dyes Pigm.* **2003**, *58*, 197–204.
29. Daniels, V. The light-fastness of textiles dyed with 6,6'-dibromoindigotin (Tyrian purple). *J. Photochem. Photobiol. A* **2006**, *184*, 73–77.
30. Lerwill, A.; Townsend, J. H.; Liang, H.; Hackney, S.; Thomas, J. A versatile microfadometer for lightfastness testing and pigment identification. In *Optics for Arts, Architecture, and Archaeology, Proceedings of SPIE 6618, Munich, Germany, Jun. 20–22, 2007*; Fotakis, C., Pezzati, L., Salimbeni, R., Eds.; Society of Photo-Optical Instrumentation Engineers: Washington, 2007; 66181G.1–66181G.12.
31. Batista-dos Santos, A. F. Los tejidos labrados de la España del siglo XVIII y las sedas imitadas del arte rococó en Minas Gerais (Brasil). Análisis formal y analogías; Ph.D. Thesis, Universidad Politécnica de Valencia: Valencia, 2009; pp. 709.
32. Whitmore, P. M.; Pan, X.; Bailie, C. Predicting the fading of objects: identification of fugitive colorants through direct nondestructive lightfastness measurements. *J. Am. Inst. Conserv.* **1999**, *38*, 395–409.
33. Billmeyer, F. W.; Saltzman, M. *Principles of Color Technology*; John Wiley and Sons: New York, United States, 1981; pp. 240.
34. Johnston-Feller, R. *Color Science in the Examination of Museum Objects: Non Destructive Procedures*; The Getty Conservation Institute: Los Angeles, United States, 2001; pp. 384.
35. Sharma, G. Color fundamentals for digital imaging. In *Digital Color Imaging Handbook*; Sharma, G., Ed.; CRC: Florida, 2002; 1–114.
36. Berger-Schunn, A. *Practical Color Measurement, a Primer for the Beginner a Reminder for the Expert*; John Wiley and Sons: New York, United States, 1994; pp. 192.
37. Whitmore, P. M. Pursuing the fugitive: direct measurement of light sensitivity with micro-fading tests. In *The Broad Spectrum: Studies in the Materials, Techniques and Conservation of Color on Paper, Chicago, United States, Oct. 5–9, 1999*; Stratis, H. K., Salvessen, B., Eds.; Archetype: London, 2002; 241–243.
38. Giles, C. H. The fading of colouring matters. *J. Appl. Chem.* **1965**, *15*, 541–550.
39. Baxter, G.; Giles, C. H.; Lewington, W. J. Relation between physical state and rate of fading of dyes. *J. Soc. Dyers Colour.* **1957**, *73*, 386–392.
40. Giles, C. H.; Baxter, G.; Rahman, S. M. Studies of high fastness to light in colouring matters in hydrophilic substances. *Text. Res. J.* **1961**, *31*, 831–844.
41. Cristea, D.; Vilarem, G. Improving light fastness of natural dyes on cotton yarn. *Dyes Pigm.* **2006**, *70*, 238–245.
42. Zahri, S.; Belloncle, C.; Charrier, F.; Pardon, P.; Quideau, S.; Charrier, B. UV light impact on ellagitannins and wood surface colour of European oak (*Quercus petraea* and *Quercus robur*). *Appl. Surf. Sci.* **2007**, *253*, 4985–4989.
43. Sundaryono, A.; Nourmamode, A.; Gardrat, C.; Grelier, S.; Bravic, G.; Chasseau, D.; Castellan, A. Studies on the photochemistry of 1,7-diphenyl-1,6-heptadiene-3,5-dione, a non-phenolic curcuminoid model. *Photochem. Photobiol. Sci.* **2003**, *2*, 914–920.