Environ. Sci. Technol. **2003**, *37,* 5687−5694

Disposable Indicators for Monitoring Lighting Conditions in Museums

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Photoinduced alterations of light-sensitive artifacts represent one of the main problems that conservators and curators have to face for environmental control in museums and galleries. Therefore, increasing attention has been recently devoted to developing strategies of indoor light monitoring, especially aimed at minimizing the cumulated light exposure for the objects on exhibit. In this work a prototype of a light dosimeter, constituted by a photosensitive dyes/polymer mixture applied on a paper substrate, is presented. This indicator, specially designed for a preventive assessment of the risk of damage for highly light-sensitive objects, undergoes a progressive color variation as its exposure to the light increases. Different, easily distinguishable color steps are exhibited depending on the light dose received, so that the dosimeter can be used straightforwardly to have a first, instrumentation-free estimation of the total light exposure. A reflectance spectroscopy study in the 350−860 nm range was carried out on prototype dosimeters exposed to light emitted from a tungsten−halogen lamp to investigate the response of the dosimeter to the light and to study the fading mechanism. Two different approaches were evaluated for the calibration of the prototype: colorimetry and principal component analysis of the reflectance spectra. The usefulness of the two methods in providing a quantitative indication of the light dose received was evaluated.

1. Introduction

In the museum environment, a minimum light level is necessary to enable visitors to fully enjoy the art objects on display. [Scientifically speaking, the term "light" refers exclusively to the visible radiation.] However, light is damaging, as, based on photolysis and photoredox reactions, alone or in combination with other environmental parameters (temperature, humidity (*1*), pollution, etc), it initiates fading, discoloration, and deterioration in a wide range of artifacts belonging to the cultural heritage. The photochemical damage is related to the radiation wavelength: the relative spectral sensitivity of a material decreases exponentially as the wavelength increases (*2*−*4*). Moreover, the damage is determined not only by the radiation energy, but also by the degree to which each wavelength is absorbed by the object (*5*). The amount of energy needed to produce a visible change may involve a variable time span, from days to years, depending on each individual material and on the environment. However, the damage incurred is always cumulative and irreversible. The net photochemical effect is the result of the total exposure that an object receives, which is the product of the illuminance and time. This concept is expressed by the "principle of reciprocity" (*6*), according to which an illuminance of 100 lux for 5 h produces the same effect as 50 lux for 10 h.

The total exposure is normally measured in irradiance units ($W \cdot cm^{-2}$). Nevertheless, in the museum environment, for the sake of convenience, it is customary to use the "light dose" (LD), measured in lux × hours (lux·h) units.

The recommendations of museums and archives in terms of the lighting of sensitive objects most often follow precise and strict guidelines (*7*−*12*). Measuring light levels can be complicated, as the light often comes from mixed sources (artificial and natural), and thus is subject to daily and seasonal changes. Lux meters and UV meters are not totally adequate, as they provide single measurements of physical entities (such as illuminance) from which an extrapolation to the cumulative exposure (LD) is often uncertain. Accurate evaluations can be achieved using data loggers, i.e. electronic monitoring cells, which yield visible-LD and UV-LD, as well as humidity and temperature measurements. However, allocating one such instrument close to each artifact on display would be cumbersome to manage and too expensive even to the wealthiest institutions. Moreover, despite the simplicity of use of recent devices, the main problem remains the interpretation of the huge amount of data recorded, during given periods, for each physical parameter. Only suitable treatments and reduction of the records could provide readable, meaningful indications on the global environmental conditions.

As an alternative approach, light "indicators" or "dosimeters", i.e. light-sensitive substrates, which exhibit a damage function similar to that of the object, can be used as sacrificial material for monitoring the damage at very low-cost. Ideally, the response of the light indicator should be quantifiable as well as faster than that of the object, thereby enabling an "early-warning system" for light damage. Moreover, the device should be small, discrete, and user-friendly, to follow any given artifact on display—even in traveling exhibitions—without disturbing the exhibit aesthetics, and accurately inform the lender institutions about the "illuminance history" experienced by the object.

In the past, several attempts have been made to characterize lighting conditions with dosimeters in museums, the first of which was adapted from the international classification of light stability for modern textile colors. This classification is based on the blue wool standards (BWS) (*13*), a set of special wool fabrics, dyed with blue dyes of increasing light-fastness, numbered 1 through 8. The BWS are sometimes used in museums (*14*, *15*), but their sensitivity range is not adapted to monitoring low exposures, as in the case of highly light-sensitive artifacts. Indeed, even the most light-sensitive BWS, no .1, does not exhibit appreciable color variation below

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10.1021/es0304401 CCC: $25.00

relatively high LDs (of the order of 100 K lux•h). Paper dyed with Rhodamine B (*16*) or cellulose acetate impregnated with crystal violet (*17*) have also been proposed to monitor LD. These alternatives to BWS, however, have never reached any degree of acceptance within the museum community at large. Quite recently (*18*), tempera-painted dosimeters were proposed for environmental indoor monitoring, but most of the dyes/pigments therein employed were suitable only for objects that are sufficiently light-fast in the medium long term, such as tempera or oil paintings. Instead, for highly light-sensitive artifacts, such as photographs, watercolors, or light fugitive dyed textiles, there is still a real need for a new light indicator able to respond significantly enough to low and very low exposure levels.

The research described here was carried out as part of an interdisciplinary project aimed at developing new tools for light monitoring in museums (*19*). Within this project, several devices with different ranges of sensitivity to light, that will palliate the lack of sensitivity of BWS, are under study. One prototype of these “dosimeters”, or “light indicators”, is presented here. This dosimeter is composed of a mixture of two dyes in a polymer matrix applied on a paper substrate. Initially blue, it successively changes its color to purple, pink, and white under the effect of light. The color change versus the LD in different experimental conditions was examined in a previous study using the CIELab* System and optical density measurements (*20*). Although light is the leading parameter for determining discoloration, several other physical/chemical factors were found to concur in the fading process. Hence, in practical use, the dosimeter is conceived as a tool for monitoring the aggressiveness of the complex environmental conditions.

The aim of the present study is to investigate the suitability of these dosimeters for a quantitative evaluation of the environmental damage of light-sensitive objects. This requires a proper calibration of the response of the dosimeter to increasing LD, which would enable to relate a given color change to a given light exposure.

The analysis was mainly devoted to obtaining an exhaustive knowledge of the indicator’s light-induced alterations, and to studying features of the fading process, by investigating, in particular, the response to various illuminances.

With the final aim of setting up suitable color scales to be used as a template for the color span displayed by the indicator, spectroscopic analyses of artificially light-aged color reference scales were carried out seeking the most adequate calibration method. Indeed, a reliable calibration curve would allow evaluation of the exposure of an object simply by following the variation in a suitable spectral parameter of the dosimeter. Ultimately, for the end-user, a simple visual inspection of the hue should reliably indicate, in a fashion analogous to that of a pH indicator, the range of LD that has affected the dosimeter and, hence, the LD that has affected the artifact on display.

2. Experimental Section

The light indicators are made of a light-sensitive layer, composed of a mixture of dyes embedded in a polymer matrix, applied on a nonabsorbent paper substrate (a bleached chemical pulp commercially sold under the name “Bristol”). Aqueous solutions of toluidine blue O (Aldrich) (5 g L^{-1}), and Eosin (Réactifs RAL) (3.96 g L^{-1}) are mixed with a polyvinyl acetate (PVAc) homopolymer emulsion (N 385 Savatex, Sté Raoul Labord). This mixture is applied on the paper substrate by spin-coating. The light indicators are dried in the dark at ambient conditions. The thickness of the coating is, on average, 100 μm. The exact composition of the light indicator (materials and know-how) is described in the French Patent FR2784458 (*21*).

A set of specimens, referred to as *reference color scales*, was obtained by exposing the light indicator to tungsten−halogen light. Other light sources such as natural and fluorescent had been previously investigated and the results were reported elsewhere (*20*). However, in the present study, only halogen light with UV filtering, the most commonly used light source in museums, was tested. Indeed, the targeted application of the light indicator is geared toward very-light-sensitive artifacts that would normally not be exhibited in a museum context under high-intensity output light with significant UV component. The 12-V light bulbs (OSRAM) were 10 and 35 W power, and with color temperature 3000 K. They were made of doped quartz crystal that blocks the UV radiation, totally in the range 300−350 nm, and partially (50%) in the range 350−380 nm. The experiments were carried out in a climate chamber at stable values of temperature (23 °C) and relative humidity (50%). Because preliminary spectral characterizations of the dosimeter showed that the material does not exhibit absorption bands in the NIR region, the use of dichroic mirrors to block the IR component of the radiation was considered unnecessary. Indeed, a setup with bare bulbs was preferred in order to ensure optimal homogeneity of the illumination field impinging the samples.

To modulate the luminous flux intensity to the desired level, optical density gray scale filters or “sensitometric strips” of various optical density were used. These gray scale filters were superimposed on the indicators during the exposure in the light chamber. The gray scales filters were strips of cellulose triacetate black and white photographic film (Kodak), developed so as to bear 19 areas (10 mm × 20 mm) of increasing optical density (OD) from 0.08 to 3.15. These allowed transmitted light from 0.07% to 83.6%, even if the practically useful range resulted slightly reduced to 14 OD areas. This exposure system resulted in 14 sections, that corresponded to 14 different LD, on the same light indicator strip, using only one exposure time.

Three reference color scales were produced by exposure to various luminous flux intensities and time spans: 50 lux during 2659 h, 100 lux during 1580 h, and 300 lux during 744 h, so that a final LD of the same order of magnitude was obtained in the three scales. This was done in order to evaluate how closely the system followed the reciprocity law.

The spectral response of the light indicator to different lighting conditions was investigated by considering the reflectance spectrum, collected on the different stages of each reference color scale. Hence, three sets of 14 spectra corresponding to increasing LD values and covering approximately the range 0−150 K lux•h, were comparatively analyzed.

The measurements of diffuse reflectance were performed in the 350−860 nm range, in 1-nm steps, by means of a Perkin-Elmer λ19 double-beam spectrophotometer, equipped with a 60-mm integrating sphere accessory, working in the geometrical configuration 8°/D.

A light-trap in the integrating sphere was used to exclude the specular component in the reflectance signal. The resolution of the spectrophotometer was ±0.2 nm. The instrumental calibration was made using a 99% Spectralon diffuse reflectance white reference, whereas for the wavelength calibration Holmium Oxide Spectralon standards were used.

Suppliers included the following: Sigma-Aldrich Chemie GmbH, Riedstr. 2, D-89555 Steinheim, Germany; Réactifs RAL, Bordeaux Technopolis, 33650 Martillac; Société Labord, ZI Chemin des Arpents, Saint-Germain Lès Arpajon, BP 25, 91291 Arpajon Cedex; and Kodak-Pathé France, 26 rue Villiot, 75594 Paris Cedex 12.

3. Results and Discussion

The light-aged samples were characterized by their reflectance spectrum. This choice answers a 2-fold purpose, since the reflectance spectrum is a tool for investigating light-induced spectral alterations, and, at the same time, it makes possible the colorimetric analysis, which is useful in objectively expressing the visual perception of the color exhibited. First, the reflectance data were treated with the aim of identifying the spectral features that were mainly affected by the action of light. Thereafter, the spectral data were used to calculate the colorimetric coordinates of the color hues through which the light indicator evolves as the exposure increases. The final goal of the entire analysis was to reach a reliable calibration of the light-indicator prototype, by attributing to each color stage a mean value of the LD received, together with the corresponding tolerance interval.

3.1 Analysis of the Fading Process. The spectral behavior of the material under investigation can be characterized by considering its absorption features. Under certain conditions, these features can be inferred by expressing the reflectance data in Kubelka−Munk (KM) units. Although the KM theory is based on several theoretical assumptions, this phenomenological model is commonly adopted to treat the diffuse reflectance from matte surfaces, despite the nonideality of most real samples. The KM function, *F*(R_∞), allows relation of the easily measurable diffuse reflectance R_∞ to the ratio, k/s, between the absorption (k) and the scattering (s) coefficients, according to the following relationship (*22*):

$$F(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{k}{s} \qquad (1)$$

where R_∞ is the reflectance of a layer of infinite thickness. In principle, for a given wavelength of the incident radiation, the function $F(R_\infty)$ can be assumed to be linear with the concentration C of the absorbing component embedded/diluted in a nonabsorbing matrix, provided that the scattering coefficient s is independent of the concentration. The system under analysis was considered to fulfill the main conditions for applying the KM theory. Indeed, the samples can be assumed to have an infinite optical thickness, because no contribution to the reflectance signal arose from the back support of the active layer, as could be verified in preliminary tests. Moreover, the active layer of the dosimeter can be schematized as a homogeneous system in which particles absorbing/scattering the light are dispersed in the polymeric matrix. No anomalies due to the presence of strong absorption bands were observed in the spectra and the KM model was considered adequate to describe the system.

In the present case the absorbing material of the light indicator is a mixture of two dyes. Therefore, two different species concentrations concur in the fading process and have to be followed. The plot of the KM functions relative to the spectral data collected on the stages of the 100-lux-aged reference color scale is reported in Figure 1.

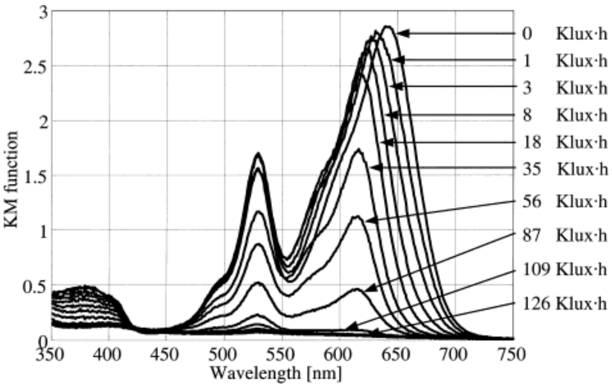


FIGURE 1. Reflectance data expressed in Kubelka−Munk units relative to the different stages of aging in the reference color scale aged under 100 lux.

TABLE 1. Results of the Best Fit of the Experimental Data Collected on the Reference Color Scales Aged Under 50, 100, and 300 lux by Using Equation 2 for the KM Peaks of the Red and Blue Dye Bands

			Red Dye		
	A_r	A_r SE	k_r [K lux h^{-1}]	k_r [K lux h^{-1}] SE	R
50 lux	1.58	0.02	0.025	0.001	0.997
100 lux	1.71	0.03	0.021	0.001	0.996
300 lux	1.59	0.02	0.019	0.001	0.997
			Blue Dye		
	A_b	A_b SE	k_b [K lux h^{-1}]	k_b [K lux h^{-1}] SE	R
50 lux	2.77	0.03	0.043	0.002	0.998
100 lux	2.89	0.03	0.029	0.001	0.998
300 lux	2.79	0.04	0.031	0.002	0.997

As can be observed, for each step of aging, the KM function was characterized by two main bands, well-separated and similarly structured (a main peak plus a shoulder). These bands are clearly related to the two dyes: the "red dye" band, with the main peak at approximately 520 nm, and the "blue dye" band, with the peak located in the 610−630 nm region. More precisely, a slight shift of the position of the blue-dye peak was observed for greater exposures, toward shorter wavelengths. The spectral evolution due to the increasing exposure to the light was investigated. The most remarkable aspect was that the peak intensities decreased as the LD value increased. The two peaks remained distinct in each spectral profile, which corresponded to a certain aging stage. This fact suggests that, at least in a first approximation, the two dyes used in the mixture did not interact with each other during the fading process. On the basis of this observation, the concentration of each single dye—and its evolution under the action of light—can be estimated by evaluating the KM peak intensity at the two maxima abscissas. The fading mechanism of the light indicator can thus be investigated by studying the disappearance rate of the dyes, that is, by examining the peak decays as the LD increases.

In Figure 2a and b the intensity of the KM peak plotted against the light dose received is reported for the "red" and "blue" dye bands, respectively. All the three color reference scales analyzed showed a similar behavior, though a slight difference occurred between the absolute values of the spectral intensities. Nevertheless, in all the specimens the "blue" and "red" dyes appeared to follow a similar decay under the action of light. To simplify the treatment of the fading mechanism, kinetic of the first order was assumed to characterize the photochemical reaction of each dye, and a best fit of the experimental data set was performed using the eq 2:

$$I(D) = Ae^{-kD} \qquad (2)$$

where $I(D)$ represents the intensity value of the KM peak and D is the LD, expressed in K lux·*h*. It should be pointed out that this is a simplified model, as a rigorous treatment of the problem should take into account a more complex law of decay, due to the complexity of the system dyes/polymer (*23*). Nevertheless, this model allows us to evaluate the values of the constants k and A for the blue and the red dyes, providing a quantitative comparison of their light-fastness. In Table 1 the results of the fitting procedure applied to each specimen of reference color scales are reported. By averaging

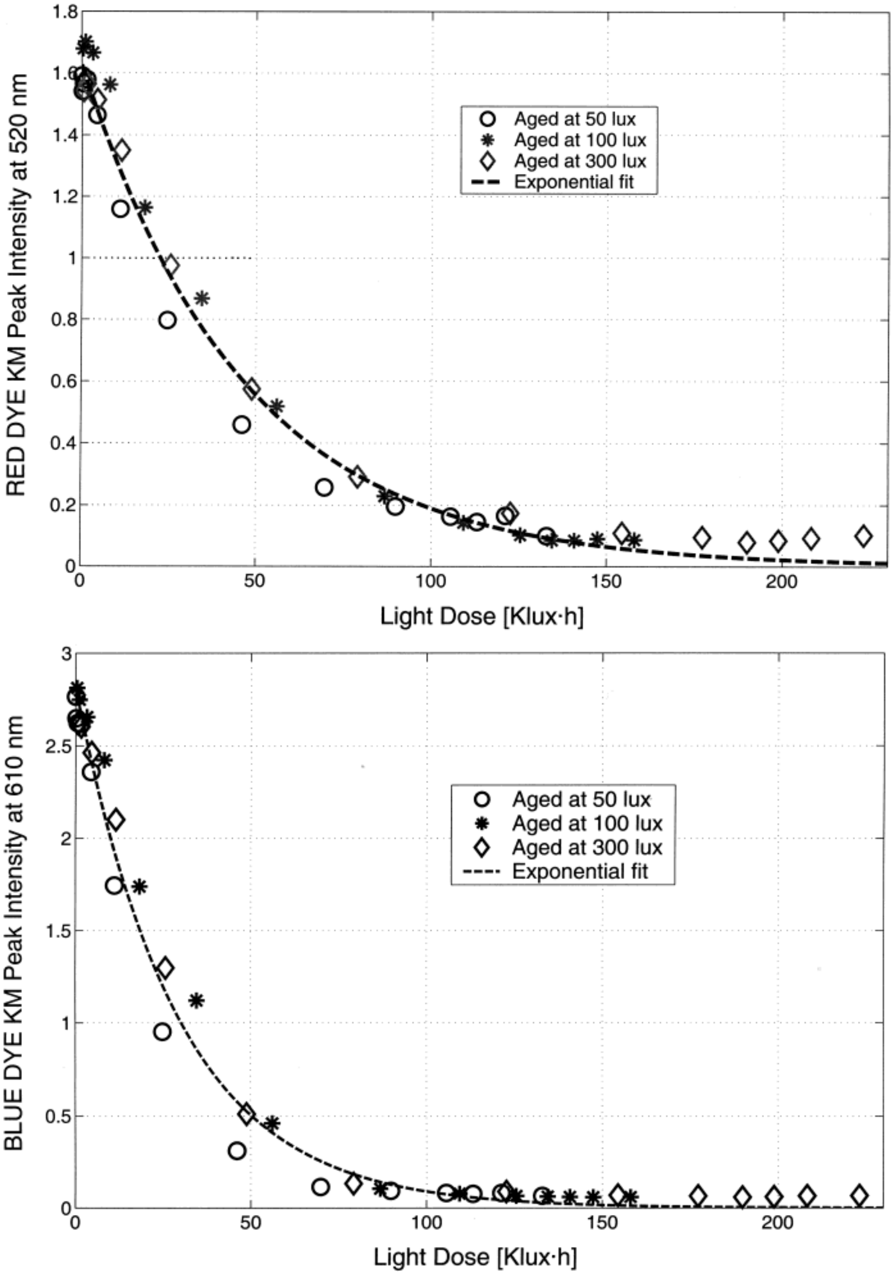


FIGURE 2. Decay of the Kubelka−Munk peak intensity against the light exposure for the “red” (a) and “blue” (b) dyes contained in the mixture used for preparing the light indicator.

the values reported in this table, eq 2 for each dye becomes

$$I_r(D) = 1.7e^{-0.021D} \qquad \textit{Red dye} \qquad (3a)$$

$$I_b(D) = 2.8e^{-0.034\,D} \qquad \textit{Blue dye} \qquad (3b)$$

The value of the constant A gives an indication of the initial concentration of the dye present in the mixture. Considering the ratio k_b/k_r, it can be seen that the blue dye fades faster than the red one by a factor of about 1.6. Furthermore, by using the reciprocal values of k_i, it is possible to define a “characteristic dose”, D_i^C, for each dye, as follows:

$$D_r^C = 1/k_r \cong 50\ \text{K lux·h} \qquad \textit{Red dye} \qquad (4a)$$

$$D_b^C = 1/k_b \cong 30\ \text{K lux·h} \qquad \textit{Blue dye} \qquad (4b)$$

The value of D_i^C corresponds to the LD to which the concentration of the i-th component is diminished by a factor $1/e$, that is, reduced to about 37% of the initial one. Hence, after exposure to a LD of about $3D_i$, the i-th component of the mixture is almost extinguished. Considering the D_i^C values obtained in eqs. 4a and 4b, two different regimes of sensitivity are identifiable to characterize the light indicator on its operative range. Indeed, up to a certain exposure, both dyes are active, and the color change depends on the balance between both the two components, whereas, above a LD of about 90 K lux·h, only the red component is still reactive and concurs with the color variation.

3.2 Calibration. For practical purposes, the use of the light indicator needs a reliable calibration scale. Because the working principle is based on color changes, first, the colorimetric analysis has been applied as the most straightforward approach to calibrate the dosimeter. Such an approach presents limitations in the precision, as the exposure is estimated on the basis of a visual evaluation of the light indicator, and subjectivity factors can affect such

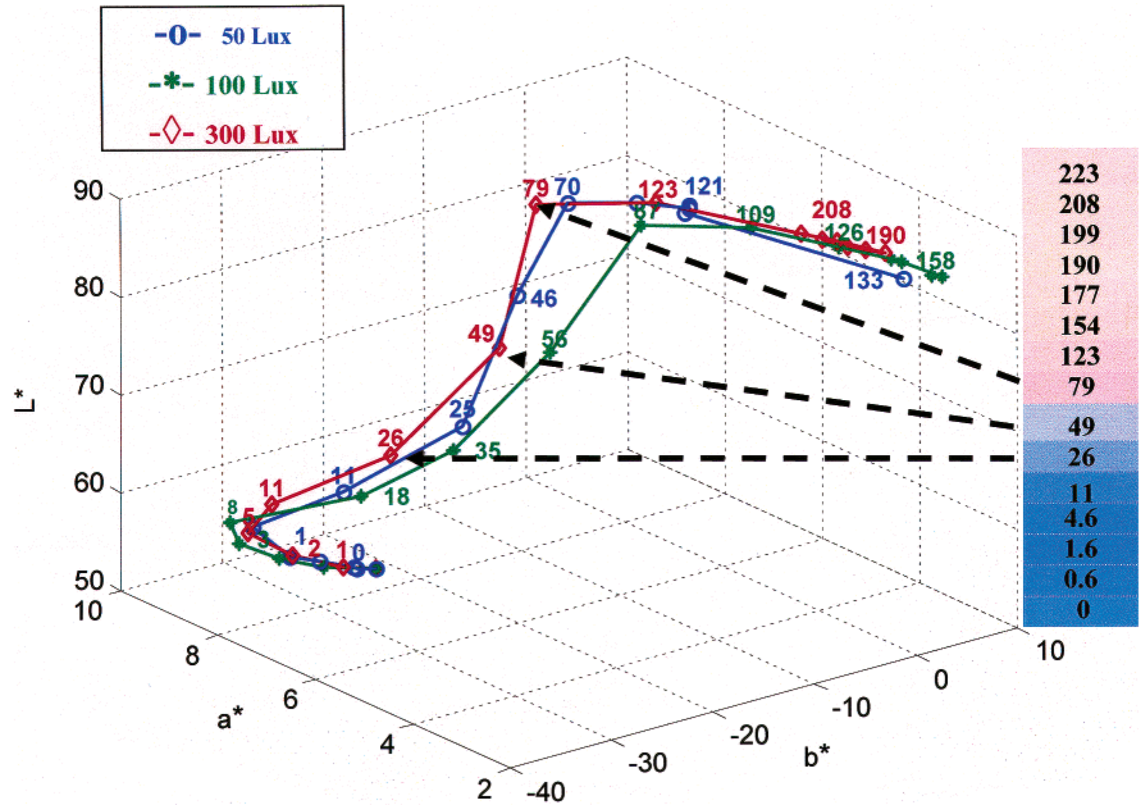


FIGURE 3. 3D representation in the *L*a*b color space of the different stages of aging of the reference color scales aged under 300 lux (red curve), 100 lux (green curve), and 50 lux (blue curve). Each data point is labeled with the corresponding LD value (in K lux·h). On the right side, the reference color scale aged under 300 lux is reproduced using the colorimetric values calculated by the measured reflectance spectrum, and the LD value relative to each aging stage is reported on it.**

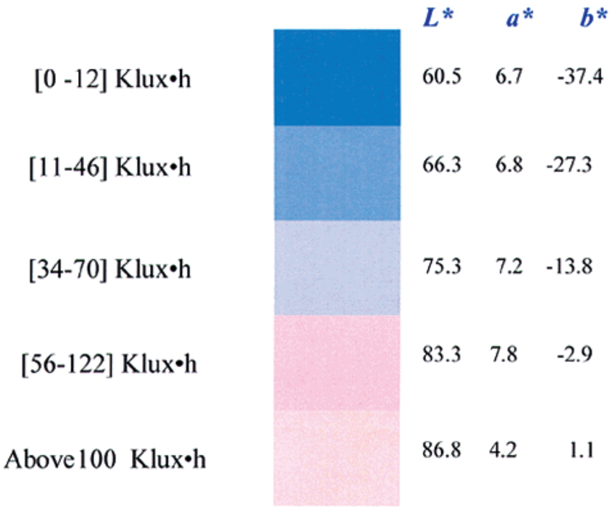
an evaluation. Nevertheless, the "colorimetric calibration" offers the advantage of an immediate relation with the exposure, without the need for instrumentation and it seems the most appropriate for an easy and fast assessment of the LD. Nevertheless, to have a more in-depth investigation and to validate the colorimetric approach, also a different calibration method, based on the principal component analysis (PCA) of the spectral data, was discussed.

3.2.1 Calibration Model Based on the Colorimetric Approach. The colorimetric coordinates relative to the different stages of aging of the light indicator have been calculated with the CIELab76 Color System (24), using the reflectance spectra of the different steps of the color reference scales. In Figure 3, the data relative to the three scales, aged under different lighting conditions, are reported in the $L^*a^*b^*$ color space. The three axes, L^*, a^*, b^*, correspond to the lightness level (L^*), the red−green ($+a^*$, $-a^*$), and the yellow−blue ($+b^*$, $-b^*$) visual stimuli, respectively. Each color step of a scale is represented by a single point. The three curves follow similar paths and a substantial correspondence between the LD values and the positions of the representative points was found. That is, a certain final color, corresponding to a given position in the $L^*a^*b^*$ color space, was determined by a given cumulative exposure. This fact suggests that the reciprocity law is obeyed in a fairly good approximation, at least within the illuminance range (50−300 lux) and for the type of light source investigated. More precisely, to judge to which extent the reciprocity is fulfilled, the practical use of the dosimeter, which is evaluated on the basis of its color, should be taken into account. It was observed that the three scales showed analogous color variations, although aged under different lighting conditions, and the system was considered to fulfill the reciprocity requirements.

To give an idea of the typical appearance of the light indicator at the different stages of aging, the entire reference color scale, aged under an illuminance of 300 lux, has been reproduced in Figure 3. As can be seen, the light indicator exhibits a gradual and continuous color variation as the LD spans the range [0−220 K lux·h]. Actually, an intrinsic uncertainty affects the attribution of a dose to a color, since the three reference color scales predict slightly different LDs for colors that, to the naked eye, appear very close to each other. Such an uncertainty represents the main difficulty underlying the calibration procedure, that is, the correct identification of a few main hues, each one corresponding to a given range of LDs. To take into account the margin of variability of each hue selected, the colorimetric calibration of the light indicator was accomplished by considering all the data belonging to the three color reference scales as a single set. Therefore, all the spectra have been grouped together and then subdivided into five sets, corresponding to the five main distinguishable hues (from blue to the almost white) that the dosimeter exhibits during its fading process. The final colors, each identifying a hue-class, were defined by the L^*, a^*, and b^* values obtained by averaging over all the data belonging to the set. Because certain samples could not be unambiguously attributed to a certain "hue class" by means of visual inspection, the minimum color variation, ΔE^* (eq. 5), between a given sample and each color among the five classes, has been considered in order to solve the uncertain cases.

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \qquad (5)$$

Hence, a "calibration scale" consisting of five steps, each corresponding to a certain exposure, expressed as a range of LD, was obtained. The range of LD to be attributed to each step was defined by considering the minimum and maximum LD values occurring in the corresponding data set.



		L*	a*	b*
[0 -12] Klux•h		60.5	6.7	-37.4
[11-46] Klux•h		66.3	6.8	-27.3
[34-70] Klux•h		75.3	7.2	-13.8
[56-122] Klux•h		83.3	7.8	-2.9
Above100 Klux•h		86.8	4.2	1.1

FIGURE 4. Calibration scale built using the colorimetric analysis. Each color step, identified by the *L*, a*, b mean values, corresponds to a certain exposure within the LD range reported.**

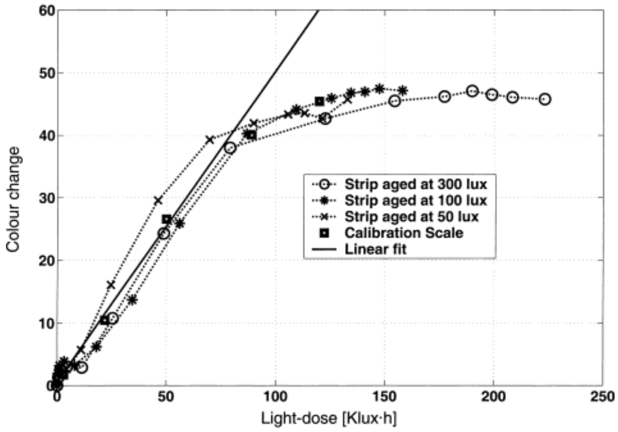


FIGURE 5. Color change, Δ*E, calculated with respect to the unexposed stage, plotted against the LD, for the three reference color scales, aged under 300 (-○-), 100 (-∗-) and 50 (-×-) lux, and for the calibration scale (◘). The solid line is the mean linear best fit.**

In Figure 4, the calibration scale of the prototype light indicator is reported, with the colorimetric coordinates calculated within the CIELab76 Color System. In this figure, the ranges of LDs of each step were defined with a partial overlapping, so that, in practical applications, also the possible intermediate hues can be referred to a certain exposure.

In the most basic application of the indicator, that is as “early-warning” system; the calibration color scale reported in Figure 4 can be visually compared with the light indicator exposed close to the object monitored, and the LD received is expected to fall in the LD range associated with the closest matching color in the scale. Alternatively, when a more objective evaluation of the dosimeter is required, the color variation (ΔE^*), calculated with respect to a reference unexposed sample, can be used to “quantify” the light-induced alteration as a function of the exposure. Practically, provided that the measurements are carried out under the same experimental conditions, the ΔE^* obtained in the dosimeter can be compared with the ΔE^* characteristic of a given step in a color reference scale for which the exposure is known.

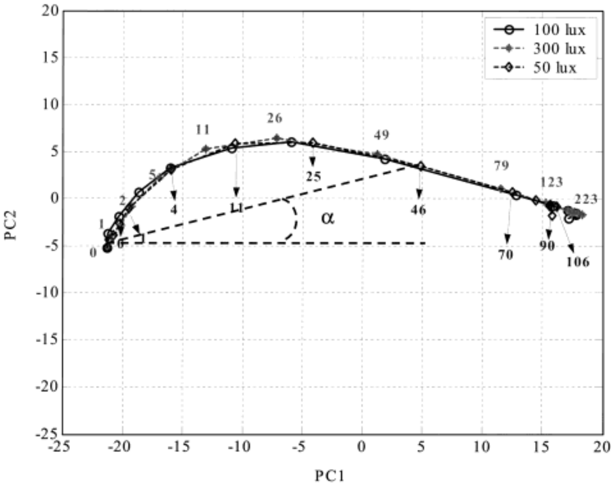


FIGURE 6. PC1−PC2 score plots for the three reference color scales aged under 300 (-∗-), 100 (-○-), and 50 (-◇-) lux. The data points relative to the 300 and 50 lux aged scales are labeled with their corresponding LD value (in K lux·h): arrows indicate the 50 lux aged sample. The angular coordinate α can be used to identify each point along its curve, as shown for the data point of LD 46.

In Figure 5 the plot of ΔE^*, calculated as the color difference between each stage of a color reference scale and the reference unexposed, is reported against the LD, for the 50, 100, and 300 lux aged reference color scales and for the five steps of the calibration scale. As can be seen, the ΔE^* behavior is almost linear until a plateau is reached, which corresponds to almost complete bleaching of the light indicator. The five stages of the calibration scale were found to closely follow the average trend of all the three scales and to faithfully reproduce the main steps of the color variation of the light indicator. Furthermore, for moderate exposures, falling within the linear part of the curve, the best fit equation of the data

$$\Delta E^* \cong 0.6 + 0.5D \tag{6}$$

can be used to assess the LD value, which can be considered appropriate in the 0−90 K lux·h range, with an uncertainty level of about 20%.

3.2.2 Spectral Analysis for Calibration Purposes: A Model Based on the Principal Component Analysis. In an attempt to obtain a deeper insight into the alteration mechanism of the indicator under the action of light, a study based on the principal component analysis (PCA) was performed. Though the results turned out to be irrelevant for the present specific data, PCA was mainly aimed at developing a different calibration methodology to be used for validating the colorimetric analysis. Furthermore, in view of future applications, the purpose was to explore more general approaches, suitable to deal also with other such prototypes.

To identify proper variables related to the light-aging process to be used as calibration parameters, the PCA was applied to suitably normalized spectral data. The reflectance spectra collected on the three light-aged reference scales were therefore pretreated by dividing the spectrum of each stage, aged at a given LD, by that of the unexposed stage (reference). The profile thus obtained is referred to as *relative reflectance spectrum* and its spectral features are specifically related to the light-induced variations with respect to the initial stage.

The examination of the total spectral variance on the set of relative reflectance data showed that 99.8% of variance was distributed between PC1 (96.2%) and PC2 (3.5%). Therefore, it was concluded that the experimental data could be exhaustively represented in a 2D space by using the first two PCs. In Figure 6 the three reference color scales have been reported in the PC1−PC2 plane. As can be observed, the scales described similar curves, overlapping each other. This confirms that an analogous spectral evolution characterized the fading process in the three samples aged at different illuminances (300, 100, and 50 lux). The noticeable aspect is that, for each curve, the data points appear to be ordered by the LD value along the path. Therefore, the position along the curve can be related to the exposure received and can be considered as a calibration parameter. To display the relationship between the position on the PC1−PC2 curves and the LD, a single coordinate, angular, can be introduced, which univocally identifies each point along its curve. The angle α (Figure 6) is subtended by the position-vector originating from the stage LD = 0 on the curve and the horizontal axis. According to this definition, in the limit of null dose ($D \rightarrow 0$), the angle α tends to 90°. Once the experimental data points are reported against the LD, it is possible, by applying a best fit procedure, to analytically express the dependence $\alpha = \alpha(D)$, and use it for calibration purposes. In the present data set, an exponential law was found to fit the experimental points.

The most interesting aspect is that the curves in Figure 6 can be used as a calibration tool by projecting on them the PCA data of samples aged under unknown conditions, and the light exposure can be estimated by their position along the curve. Nevertheless, two aspects should be taken into account in applying such a procedure. The first is the implicit hypothesis that, in the PC representation, the spectra of samples aged under unknown conditions fall along the same path as the artificially aged scales. This fact implies that the naturally aged dosimeters, exposed in museums, should exhibit spectral alterations similar to those characterizing the artificially aged reference color scales. Preliminary tests (19) have shown that such an assumption is fulfilled, provided that the environmental conditions experienced by the light indicators are close to those of the artificial aging. In other words, an evaluation of the samples aged *in field* based on the artificially aged ones is sound if the artificial light aging process can be assumed to mimic approximately the indoor conditions.

The second aspect concerns the slight discrepancy occurring between the 50 lux aged and the two other (100 and 300 lux) scales. As can be seen from the nominal LD values reported in Figure 6, the LDs in the 50-lux scale appear to be systematically shifted ahead along the "alteration path" represented by the PC1−PC2 curve. At this stage it is brought to the reader's attention that a slight tendency of color recovery has been observed when the indicator was exposed to very high illuminances of about 100 K lux (25). However, this phenomenon was never observed in the range of interest (50−300 lux), and cannot therefore account for that small discrepancy observed. More likely, the latter can be explained by small experimental variations, due to the empirical procedure followed in fabricating the color reference scales. Summarizing, because of the slightly different predictions of the reference color scales, an intrinsic uncertainty about the exposure estimation still exists, even adopting a calibration method based on the PCA. Analogously to the colorimetric approach, the PCA based calibration can only allow subdivision of the operative range [0−100 K lux·h] of the dosimeter in only a few (no more than 5) intervals of LD, of finite width. Each interval, corresponding to a given section on the curve, can thus be attributed to a certain stage of aging of the dosimeter.

It can be concluded that the PCA analysis fully validated the results obtained by the colorimetric analysis, showing in particular that, in the present case, no significant improvements in the accuracy of calibration were obtained by a more refined treatment of the spectral data.

A comparative examination showed that the two methodologies developed (colorimetric analysis and PCA) were consistent, as both allowed correlation of the fading process with the LD received by the light indicator with a similar confidence level. In particular, it was possible to determine the LD ranges within which the color spans successively in the blue, purple, pink, and white hues.

Measurement of the total color variation ΔE^*, on one hand, corroborated that a simple visual inspection could be reliably used, and, on the other hand, yielded more precise information on reciprocity phenomena. Moreover, since the total color variation was found to follow a strict linear behavior against the LD in the range 0−90 K lux·h, the parameter ΔE^*, as a result, was found appropriate for calibrating the dosimeter.

The PCA approach provided a different representation of the alteration path occurring in the dosimeter with the increase in the LD. It showed that a single calibration parameter was sufficient, as first approximation, to express the spectral variation as a function of the LD received. Consequently, the light indicator was clearly found to respond mainly to the LD received. This confirms its usefulness for the targeted purpose in the museum community, as an early warning system providing an assessment of the risk factor related to light. Nevertheless, also other parameters − such as temperature, humidity, and spectral distribution of the light source − may have an influence on the color change. Therefore, the typology of dosimeter proposed should be regarded as an "integrating" environmental indicator.

Acknowledgments

This work was supported by the EC Project "LiDo" (A light dosimeter for monitoring cultural heritage: development, testing and transfer to market, EVK4-CT-2000-00016), under the Fifth Framework Program. We thank Dr. Hannelore Roemich (Fraunhofer Institut fur Silicatforschung − Bronnbac, Germany) for fruitful discussions and useful comments.

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Received for review April 21, 2003. Revised manuscript received September 18, 2003. Accepted September 23, 2003.

ES0304401