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Evaluation of the museum environmental risk by means of tempera-painted dosimeters

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Abstract

The monitoring and control of environmental parameters provide useful information in order to reduce the decay of works of art. Dosimeters that reproduce the pictorial structure of paintings as closely as possible were prepared and tested to evaluate the effects induced on works of art by the "global" indoor environment. These dosimeters were aged under different conditions in ageing chambers, and successively were placed in the Uffizi Gallery for several months. The data obtained from the naturally aged dosimeters were compared with those found for the artificially aged, thus providing information on the alteration process induced by the environmental factors.

Keywords: Environmental monitoring; Visible reflectance spectroscopy; Non-invasive investigation

1. Introduction

Paintings on exhibit in galleries and museums are inevitably subject to deterioration with the passage of time. Exposure to various environmental parameters such as, ultraviolet (UV) and visible light, temperature, relative humidity (RH), particulate, atmospheric gases and pollutants are responsible for ageing painted works of art [1–7]. Colour changes are the most apparent effects of these environmental conditions. The studies of these parameters have primarily focused on the monitoring of various pre-selected factors. However, the monitoring of environmental parameters by measuring the individual factors at a particular point in times does not yield an accurate assessment of the potential damage to art since the internal environment is always subject to fluctuations. In order to obtain data on the global impact of the environment affecting the exposed artworks, the synergistic effects of the various environmental factors must be analysed. Thus, a different approach for evaluating the conditions or the change in conditions, which may alter the stability of the objects and affect their longevity, must be considered. With this approach, the paintings themselves can be studied as dosimeters integrating all the effects of the environment.

However, because of a paintings' uniqueness, the actual artworks cannot be considered "test panels", which can be subjected to harsh conditions and sampled without restriction. Therefore, mock paintings were constructed with similar materials to act as dosimeters and to serve for monitoring the quality of the museum environment.

The fading of painted artworks is one of the most immediately visible effects of the environment. Recording spectra in the visible region at different times (as before and after ageing processes) makes it possible not only to get information about the induced

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chemical changes, but also to have a direct measurement of the potential damage to the work of art. In addition, the obtained data could be better related to the actual damage occurring on paintings, since colour changes are a macroscopic and global index of alteration.

In this paper, the results obtained by non-invasive reflectance spectroscopic analysis in the visible region on mock paintings are presented. The mock-ups were artificially aged under different exposure conditions (light, thermal, and pollutant exposure). By comparing the reflectance spectra, acquired before and after artificial ageing procedures, it was possible to evaluate the mock paintings' alteration induced by the different exposures. Finally, the data obtained in the laboratory were compared with the results obtained from a mock painting (made with 12 dosimeters) that was exposed to natural ageing at the Uffizi Gallery, Florence.

2. Experimental

Several dosimeters were prepared by using different pigments/dyes (Table 1) mixed with egg tempera medium (yolk and egg white). The selected pigments/dyes were required to have a different stability to light and pollutants, to cover a wide range of colours of both natural and synthetic origin, and to be compatible with egg tempera medium. In order to obtain a constant thick painted layer (200 μm wet layer thickness), the pigments/dyes were deposited on melinex® (125 μm-thick polyethylene terephthalate sheets) using a film applicator.

The painted sheets of melinex®, one for each pigment or dye, were cut into small strips as two different sets of the same pigment/dye were essential. The first set was artificially aged and the second was used for preparing the mock paintings (dosimeters), which were exposed in natural environments (i.e. galleries and museums). Both sets had its own reference strip stored in controlled environment without oxygen and light.

The artificial ageing tests consisted of three separate exposure cycles of different environmental parameters: light (visible component only), temperature, and pollutants (SO_2, NO_x). The samples aged under light were exposed in a light box for 4, 8, 16, 32 and 64 days using Philips TLD94 58 W daylight rendering fluorescent tubes. These tubes were filtered with Perspex VE UV filters which had a cut-on wavelength at about 400 nm and maintained a constant sample illuminance of 18 klux. During this ageing process, the temperature and RH in the light-box were around 30°C and 30%, respectively. For the thermal ageing exposure the samples were placed in an oven without any lights at 60°C and at 55% RH for 7, 14, and 21 days. Exposure to air pollutants was carried out for 4 days under a continuous flow of SO_2, NO_x, and air, so that the overall concentrations of SO_2 and NO_x in the gas chamber were approximately 10 and 20 ppm, respectively ($T = 23°C$, $RH = 55\%$).

One of the mock paintings, prepared for natural ageing in museums and galleries, was placed for 9 months (from 16 December 1996 to 29 September 1997) in the Leonardo room at the Uffizi Gallery, Florence.

Table 1
Pigments chosen for the preparation of the mock dosimeters

Pigment	Source	Chemical formula
Extra fine azurite	Kremer, Germany	$2CuCO_3{\cdot}Cu(OH)_2$
Extra fine smalt	Kremer, Germany	SiO_2–K_2O–CoO
Synthetic indigo	Janssen, Belgium	$C_{16}H_{10}N_2O_2$
Mountain cinnabar	Kremer, Germany	HgS
Lead white	Aldrich, USA	$2PbCO_3Pb(OH)_2$
Lead antimoniate yellow	Zecchi, Italy	$Pb_2Sb_2O_6$(O, OH)
Raw Sienna Earth	Zecchi, Italy	αFeOOH — αFe_2O_3
Lead(II) chromate	Aldrich, USA	$PbCrO_4$
Curcumin	Acros, USA	$C_{21}H_{20}O_6$
Alizarin	Acros, USA	$C_{14}H_8O_4$

A spectrophotometer (Perkin-Elmer Mod. λ19) equipped with a 60 mm integrating sphere was used to analyse all the samples. The reflectance spectra were acquired from 360 to 2500 nm. The resolution of the spectrophotometer was ±0.2 and ±0.8 nm for the visible and near-IR ranges, respectively. Each sample was measured three times (three different cycles of measurements) in order to reduce possible errors which might be induced by external sources. Calibration was performed with plates of pressed $BaSO_4$ powder (purity >99.99%). The colorimetric data were evaluated from the reflectance spectra of the samples following the CIELAB1976 recommendation [8]. The mean error of the measurement, due to incorrect repositioning operations, non-homogeneous layers, etc., was evaluated as about $\pm 0.7\Delta E$ (colour variation) units.

These spectrophotometric measurements allowed the evaluation of the changes in the dosimeters that were induced by the artificial or the natural ageing processes as follows:

1. *Display of the difference between the reflectance spectra of the aged sample and the control* ($\Delta R\%$). $\Delta R\%$ made it possible to monitor the spectral variations related to the chromophore and/or to the scattering properties of the surface. An almost constant value of $\Delta R\%$ over the visible spectral range indicated that no change of chromophore had occurred, and the reflectance variation was mainly due to a different scattering of the investigated surface.
2. *Calculation of the colour change* (ΔE) *together with its three components* Δa^*, Δb^* *and* ΔL^*, *according to the CIELAB* 1976 *recommendation*. These data were directly correlated with the visual perception.
3. *Principal component analysis* (PCA). PCA was performed in order to stress the variability within the spectra of the artificially aged samples. To explain the spectral variation that occurred as a consequence of the natural ageing processes, the reflectance spectra collected from the exposed strips at the field site were projected onto the PCA model, which was built using the artificially aged data. The PCA algorithm was implemented in the MATLAB® environment and run on a PC.

3. Results and discussion

On the basis of the colorimetric data on the artificially aged dosimeters, they were grouped into fugitive, durable, and permanent categories for the three exposure conditions (64 days for the light; 21 days for the thermal; 4 days for the pollutant). The classification based on the ΔE between aged and non-aged dosimeters is depicted in Fig. 1. The dosimeters prepared with lead white, alizarin and lead chromate were further investigated and the obtained results are displayed in Table 2.

3.1. Lead white pigmented tempera

The reflectance spectra of the lead white reference strip, light aged 64 days, thermal aged 21 days, and pollutant gas aged 4 days, showed a small difference and this difference can be better highlighted when the reference spectrum was subtracted from the others (Fig. 2). From these data, the light exposure affected lead white spectrum in a different way with respect to temperature or pollutant gas. As expected, the same results were also determined by evaluating the integral of difference spectra (DSI), which were the differences between the areas subtended by the reflectance spectrum of a sample after ageing and of the related reference. The DSI values for the artificially aged lead white strips (Fig. 3) were well correlated with ageing time exposures for light and thermal aged sensors, while information concerning correlation with pollutant gas exposure was not available, because only one gas ageing trial was performed. However, the adopted exposure for pollutant gases (4 days) affected to a large extent this sensor.

Regarding the colorimetric study performed on these samples, ΔE mainly derived from Δb^*, the light aged samples turned towards blue hue, while the temperature and gas aged samples turned more yellow after ageing.

The PC1–PC2 scores plot (Fig. 4) was obtained by applying PCA on spectra (360–830 nm range) of lead white artificially aged dosimeters. It was evident that three groups of samples, corresponding to the different artificial ageing factors, were well distinguishable, in other words, the different ageing conditions could be discriminated by means of visible spectroscopy. In particular, PC1 well discriminated between light aged

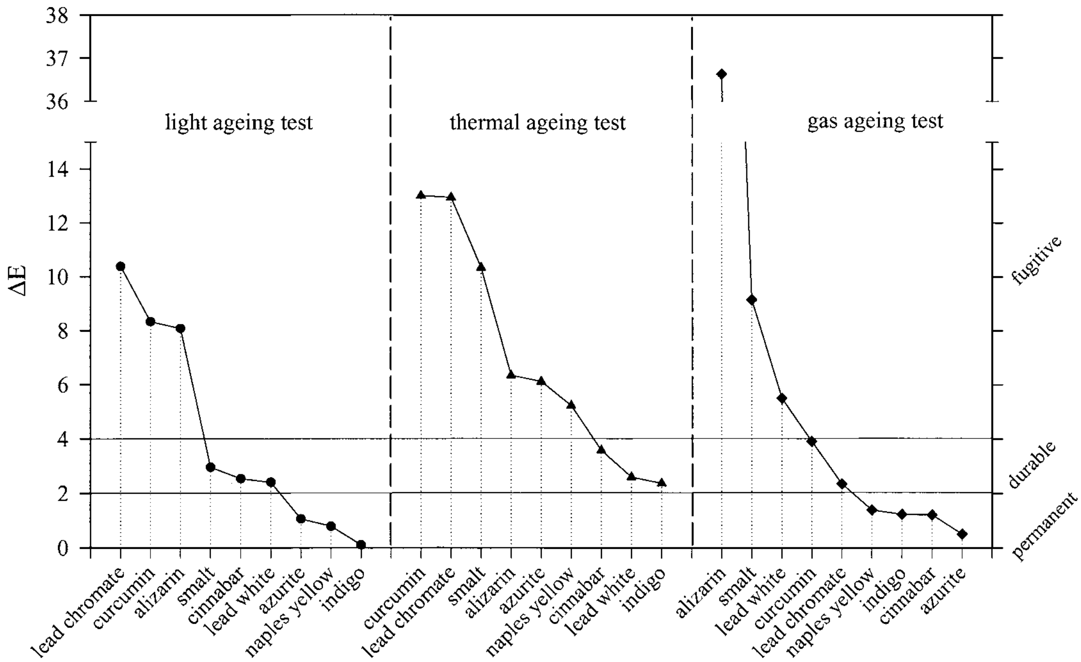

Fig. 1. Sensitivity (ΔE) of the various pigments/dyes under different ageing conditions.

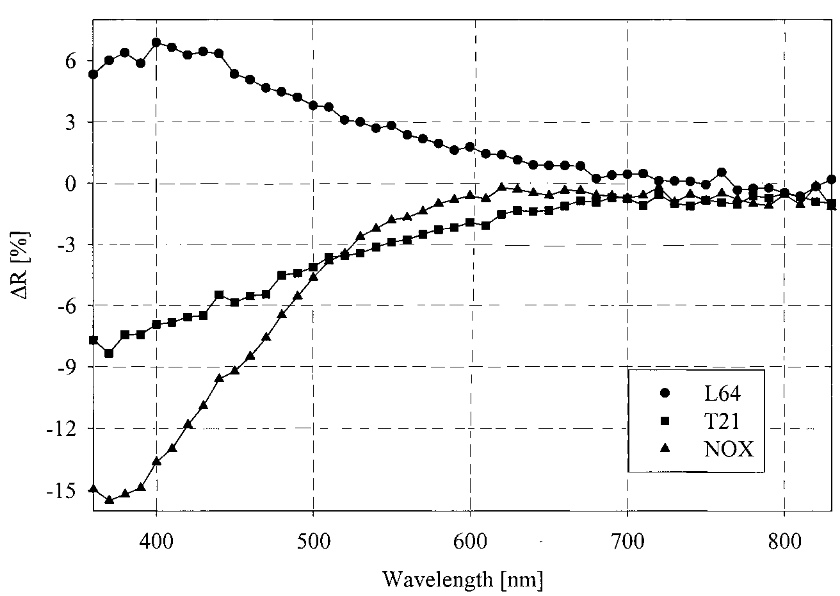

Fig. 2. Difference curve of the reflectance spectra ($\Delta R\%$) of lead white tempera dosimeters. For legend, see Table 2.

Table 2
Colorimetric values calculated on the artificially and naturally aged dosimeters

Dosimeter	Ageing process	Acronym	ΔE	Δa^*	Δb^*	ΔL^*
Lead white	Light 4 days	L04	1.0	−0.2	−0.9	0.4
	Light 8 days	L08	1.1	−0.2	−0.9	0.5
	Light 16 days	L16	1.9	−0.3	−1.6	0.9
	Light 32 days	L32	2.0	−0.3	−1.8	0.8
	Light 64 days	L64	2.4	−0.2	−2.1	1.0
	Temperature 7 days	T07	1.5	0.4	1.0	−1.0
	Temperature 14 days	T14	2.2	0.0	2.1	−0.8
	Temperature 21 days	T21	2.6	0.0	2.3	−1.2
	Pollutant gases	NOX	5.5	−0.9	5.4	−0.9
	Uffizi Gallery, Florence	UFF	2.7	−0.1	−2.4	1.2
Alizarin	Light 4 days	L04	3.2	1.0	2.9	1.0
	Light 8 days	L08	3.4	0.7	3.0	1.3
	Light 16 days	L16	4.4	1.3	3.6	2.1
	Light 32 days	L32	5.8	2.1	4.6	2.9
	Light 64 days	L64	8.9	3.6	6.9	4.4
	Temperature 7 days	T07	1.8	−1.2	−1.0	−1.1
	Temperature 14 days	T14	1.9	−1.0	−1.1	−1.2
	Temperature 21 days	T21	2.3	−1.6	−1.6	−0.6
	Pollutant gases	NOX	36.6	17.8	27.7	16.0
	Uffizi Gallery, Florence	UFF	6.1	3.1	4.3	3.0
Lead chromate	Light 4 days	L04	2.7	−1.9	−1.2	−1.5
	Light 8 days	L08	4.6	−1.2	−3.9	−2.0
	Light 16 days	L16	6.2	−4.7	−2.5	−3.3
	Light 32 days	L32	6.8	−2.8	−5.2	−3.4
	Light 64 days	L64	7.5	−3.1	−5.7	−3.8
	Temperature 7 days	T07	4.6	−2.2	−3.4	−2.3
	Temperature 14 days	T14	7.1	−3.8	−4.9	−3.4
	Temperature 21 days	T21	10.5	−5.2	−8.7	−2.8
	Pollutant gases	NOX	2.4	−1.6	1.7	−0.6
	Uffizi Gallery, Florence	UFF	9.5	−6.2	−5.5	−4.6

and thermally or pollutants aged dosimeters, while PC2 was able to differentiate the pollutants aged dosimeter from all the other sensors. A good correlation between ageing time and PC1 scores was found for light aged dosimeters.

3.2. *Alizarin pigmented tempera*

DSI (Fig. 5) showed that alizarin dosimeter was extremely sensitive to pollutants. The effect of light and pollutants ageing factors produced an increase of reflectance. On the other hand, the spectra of thermal aged alizarin sensors had a reflectance lower than reference spectrum and the changes due to this ageing factor seemed to be saturated after 7 days exposure time. The same conclusions were derived from the colorimetric analysis: the alizarin dosimeters were very sensitive to the pollutant ageing ($\Delta E = 36.6$) and sensitive to the light ageing ($\Delta E = 8.9$). The main contribution to ΔE was given by Δb^*, which was linked to a relevant increase in reflectance in the 500–700 nm range. This increase produced a shift in the colour evaluation, compared with the reference strip, towards reddish-yellow hue.

From the PC1–PC2 scores plot (99.9% of total variance), three groups corresponding to the three different ageing conditions were clearly separated (Fig. 6).

3.3. *Lead chromate pigmented tempera*

The DSI values (Fig. 7) indicated that light and thermal ageing played a different role from pollutants in the alteration process of lead chromate dosimeters. In fact, the spectral modification induced by light and

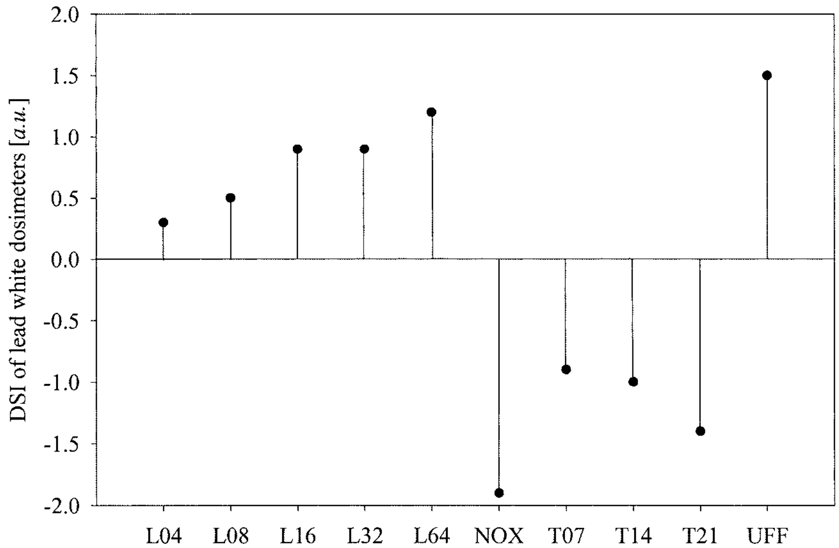

Fig. 3. DSI values for artificially and Uffizi aged lead white dosimeters. For legend, see Table 2.

thermal ageing gave a decrease of reflectance (in the 360–830 nm range) in respect to the reference spectrum, while pollutants produced a reflectance increase. Fig. 7 displays that 32 days light aged and 21 days thermal aged sensors showed a change smaller than 16 days light and 14 days thermal aged sensors, respectively. The fact that light aged DSI values were not in perfect accordance with the time exposure might have

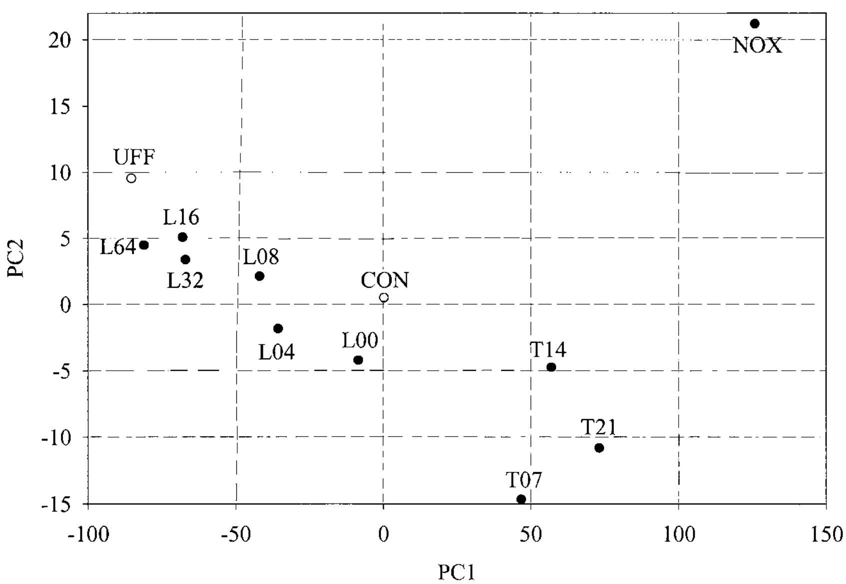

Fig. 4. PC2–PC2 scores plot of artificially aged lead white dosimeters. The reflectance spectra of Uffizi Gallery dosimeter and its reference were projected on the same diagram. For legend, see Table 2 (L00: reference for artificially aged dosimeters and CON: reference for naturally aged dosimeters).

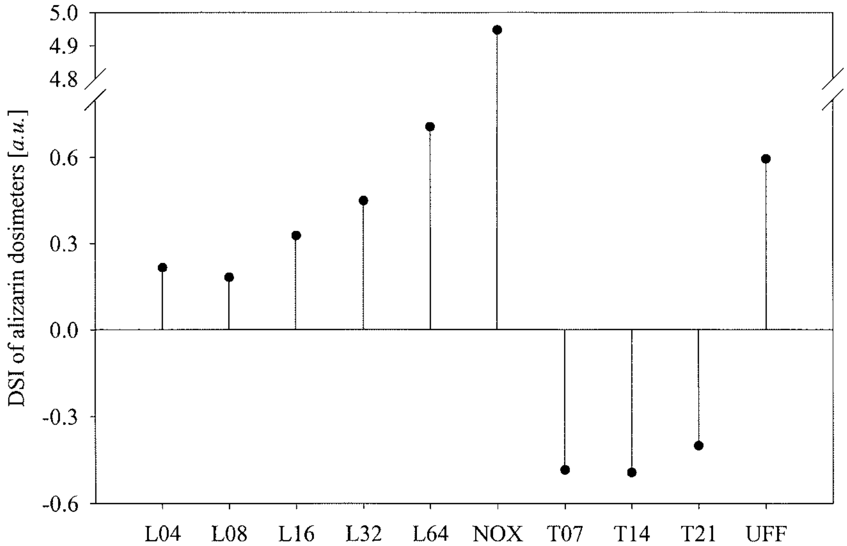

Fig. 5. DSI values for artificially and Uffizi aged alizarin dosimeters. For legend, see Table 2.

been caused by the lack of homogeneity of the painted dosimeters. Colour analysis indicated a decrease of lightness $\Delta L^* < 0$ (darkening) for all the investigated lead chromate dosimeters, and colour change (ΔE) well correlated with ageing time. PC1 divided thermal aged dosimeters from pollutants and light ones and PC2 split these latter dosimeters into two groups (Fig. 8). In particular, light aged dosimeters were spread along PC2 axis following the trend of integral values.

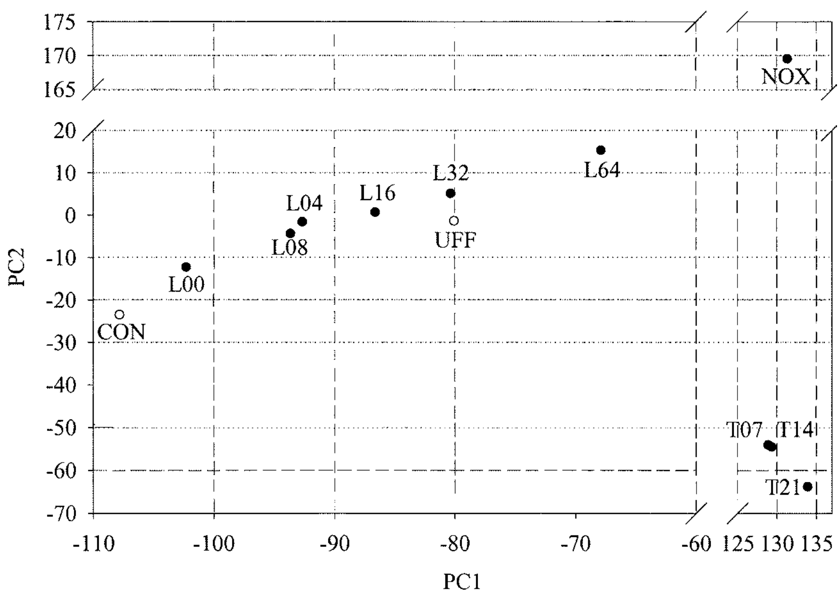

Fig. 6. PC2–PC2 scores plot of artificially aged alizarin dosimeters. The reflectance spectra of Uffizi Gallery dosimeter and its reference were projected on the same diagram. For legend, see Table 2 (L00: reference for artificially aged dosimeters and CON: reference for naturally aged dosimeters).

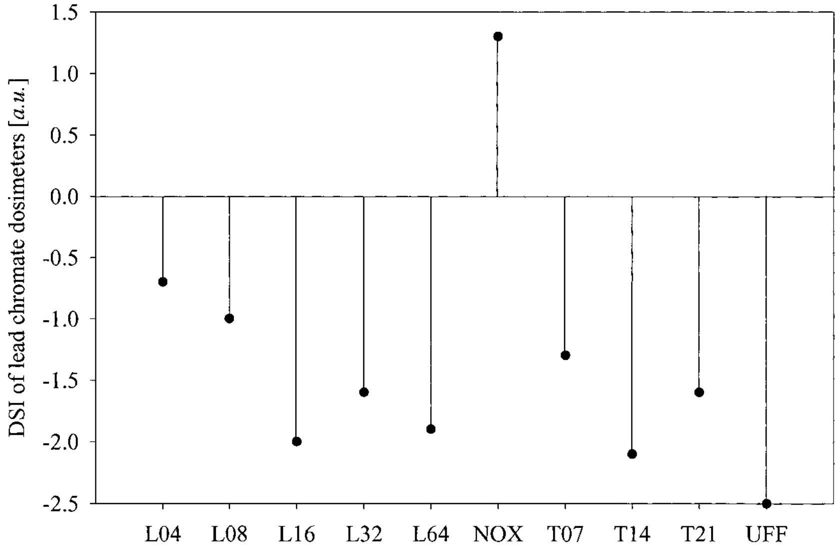

Fig. 7. DSI values for artificially and Uffizi aged lead chromate dosimeters. For legend, see Table 2.

3.4. Uffizi mock painting

The data obtained from the Uffizi mock painting were compared with the artificially aged dosimeters in order to estimate the effect of the different environmental factors.

The colorimetric values of these alizarin, lead white, and lead chromate dosimeters (Table 2),

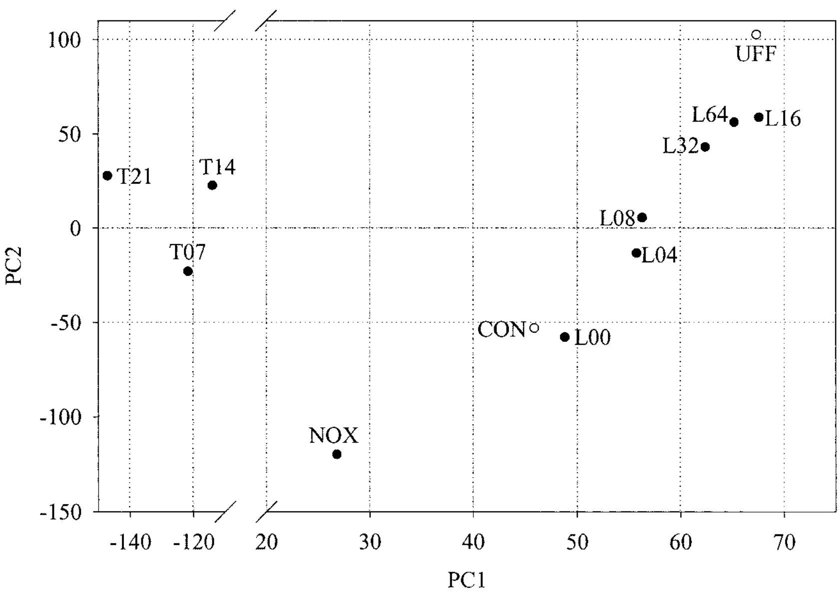

Fig. 8. PC2–PC2 scores plot of artificially aged lead chromate dosimeters. The reflectance spectra of Uffizi Gallery dosimeter and its reference were projected on the same diagram. For legend, see Table 2 (L00: reference for artificially aged dosimeters and CON: reference for naturally aged dosimeters).

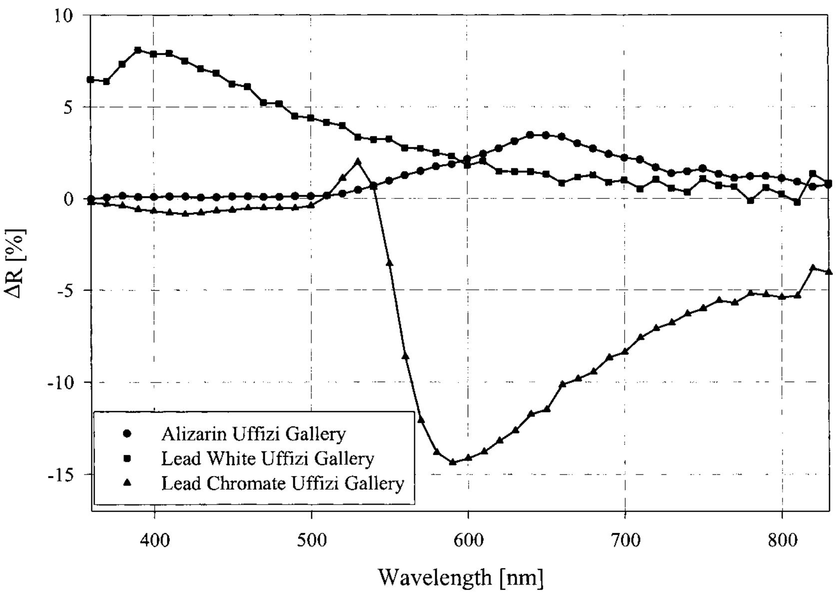

Fig. 9. Difference curve of the reflectance spectra ($\Delta R\%$) for Uffizi Gallery aged dosimeters.

denoted that the environment within the Gallery did affect the dosimeter during the 9-month exposure. For the first two dosimeters (alizarin and lead white) Δa^*, Δb^*, and ΔL^* showed a trend which excluded an effective role in the final colour variation played by the thermal-ageing process. Thus, light alone or together with pollutants seemed to be the main factor that induced colour alteration of the mock painting in the Uffizi Gallery.

Positive ΔR was found for both alizarin and lead white dosimeters, while lead chromate dosimeter displayed a small positive ΔR value around 530 nm and large negative values above 550 nm (Fig. 9). This result also confirmed the importance of light in the Uffizi ageing mechanism, and excluded a significant role for temperature, as evinced from DSI data (Figs. 3, 5 and 7, respectively).

The reflectance spectra of the dosimeters previously exposed in the Uffizi Gallery were projected in their corresponding score plot obtained by applying PCA on the artificially aged spectra (Figs. 4, 6 and 8, respectively). In particular, the alteration of the lead white and lead chromate dosimeters in the Uffizi Gallery seemed to be higher than their 64-days light exposure ageing.

4. Conclusion

On the basis of these measurements, the role of light in the Uffizi Gallery was manifest. On the other hand, the role of pollutants was uncertain. Indeed, the behaviour of alizarin and lead chromate was also in agreement with the effect of the considered pollutants, while lead white was not correlated to the effect of these pollutants. However, the effect of other pollutants (i.e. ozone, carbon dioxide, hydrogen sulphide, etc.) could be significant in natural ageing conditions.

Moreover, the proposed dosimeters provided useful information for monitoring the "global" environmental risk in museums and galleries. Starting from this experience, a suitable mock painting prepared with different pigments/dyes showing different sensitivities to the specific ageing sources is strongly recommended.

Lastly, it must be stressed that, owing to the actual nature of the dosimeters, the observed damage, though amplified, is very close to that suffered by the paintings on exhibit.

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