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DEVELOPMENT OF PORTABLE MICROFADING SPECTROMETERS FOR MEASUREMENT OF LIGHT SENSITIVITY OF MATERIALS

ABSTRACT

Microfading was originally designed for efficiently detecting extremely light-sensitive materials on objects in situ to determine the appropriate exhibition lighting conditions. By focusing an intense beam of light to a tiny sub-millimetre sized spot and simultaneously monitoring the colour change over time, the fading rate of the material can be measured without producing noticeable damage. The increased intensity of light allows rapid determination of light-fastness of materials. This paper examines an improved design of microfading spectrometer that is easy to assemble, compact, robust, capable of fully automatic acquisition of data with precision control of the fading time to produce higher precision measurements and to allow simultaneous monitoring of colour, spectral reflectance and other changes in real time. The effects of various parameters such as thickness and concentration of paint layer, the binding medium and substrate on the fading rates are examined for selected pigments and found that in certain cases substrates, binding media and thickness can affect the fading rate. Reciprocity in the context of microfading compared with realistic exhibition conditions is examined and found that it breaks down for some pigments.

RÉSUMÉ

La microdécoloration a été conçue à l'origine pour détecter de manière efficace les matériaux extrêmement sensibles à la lumière sur des objets *in situ* afin de déterminer les conditions d'éclairage appropriées pour leur exposition. En dirigeant un faisceau de lumière intense sur un minuscule point de moins d'un millimètre et en surveillant simultanément le changement de couleur au fil du temps, il est possible de mesurer la vitesse de décolora-

INTRODUCTION

Microfading is a micro-destructive technique that makes it possible to examine the light sensitivity of materials in situ, which is particularly useful when the exact composition of the material is not known. It has been used in the conservation field to compare rapidly the rate of fading of known pigment samples or other coloured materials and also to measure directly unidentified pigments on works of art that might fade if exposed to excessive light on display. Since the method causes hardly discernable damage on a micro level to only the most sensitive pigments, it is potentially a very useful way of pre-empting more extensive damage on display.

Ten years since the invention of the first microfadometer (Whitmore et al. 1999), a new microfading spectrometer with improved portability (a few kilograms) and accuracy was built in a collaboration between the Tate and Nottingham Trent University, taking advantage of the availability of compact light sources and portable fibre optic spectrometers (Lerwill et al. 2008). The instrument consists of a probe head with a 0/45° geometry using identical focusing optics in both illumination and collection. The illumination spot is slightly smaller than the measuring spot since the collection probe is at 45° to normal. The probe head needs to be aligned such that the illumination and collection spots are coincident when in focus. The probe head is placed on a motorized X-Y-Z stage such that the Z focusing is controlled by the motorized micrometer stage ensuring accurate focusing and hence high precision estimates of incident power per unit area. The motorized X-Y stage allows automated measurements of various pre-determined positions on an object or a well plate. Detailed design of the instrument was published by Lerwill et al. (2008). The repeatability of the instrument is better than $\Delta E_{00} = 0.1$ for repeat colour measurements of the same spot (Lerwill 2011). The accuracy of fading measurements is limited by intensity fluctuations of the light source which is less than 1% in 7 hours. Heating by the focused light increases the temperature by only a couple of degrees centigrade.

While the instrument has improved portability, the proper alignment of the probe head when re-assembled each time can be a non-trivial task. In addition, the motorized stages and the spectrometer are not computer controlled by the same program, the shutter is controlled manually and the focussing is not automated. This paper describes a new upgraded

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tion du matériau sans produire de dommage visible. L'intensité accrue de la lumière permet de déterminer rapidement la résistance à la lumière des matériaux. Cet article examine la version améliorée d'un spectromètre de microdécoloration facile à assembler, compact, robuste, qui permet l'acquisition entièrement automatique des données avec un contrôle précis de la durée de la décoloration, afin de fournir des mesures de précision supérieure et de permettre un contrôle simultané des variations de couleur, de la réflectance spectrale et d'autres changements avec le temps. Les effets de plusieurs paramètres comme l'épaisseur et la concentration de la couche picturale, le liant et le substrat sur les vitesses de décoloration ont été examinés pour une sélection de pigments. Les résultats indiquent que dans certains cas, les substrats, les liants et l'épaisseur de la couche picturale peuvent influer sur la vitesse de décoloration. La réciprocité dans le contexte de la microdécoloration comparée avec des conditions d'exposition réalistes a été examinée, montrant que cela ne fonctionne pas pour certains pigments.

RESUMEN

La microdecoloración se diseñó originalmente para detectar de manera eficiente materiales extremadamente sensibles a la luz en objetos in situ, y poder determinar las condiciones de iluminación adecuadas para su exposición. Enfocando un rayo de luz intensa en un pequeño punto de menos de un milímetro, y monitoreando simultáneamente el cambio de color a lo largo del tiempo, se puede medir la tasa de decoloración del material sin causar daños visibles. La intensidad aumentada de luz permite determinar rápidamente la resistencia de los materiales ante la luz. Este artículo analiza un diseño mejorado de espectrómetro de microdecoloración, fácil de montar, compacto, robusto y capaz de adquirir datos de manera totalmente automática con control de precisión del tiempo de decoloración, que permite obtener medidas de mayor precisión y hacer un monitoreo simultáneo del color, la reflectancia espectral y otros cambios en tiempo real. Se examinaron los efectos que varios parámetros, como el grosor y la concentración de la capa de pintura, el aglutinante y el sustrato en algunos pigmentos seleccionados, y se descubrió que en ciertos casos, los sustratos, los aglutinantes y el grosor pueden afectar a la tasa de decoloración. Se estudió la reciprocidad en un contexto de microdecoloración comparado con condiciones de exposición realistas y se descubrió que en el caso de algunos pigmentos se rompe.

microfading spectrometer with improved portability and simplicity in the probe design as well as being fully computer controlled.

THE UPGRADED MICROFADING SPECTROMETER

Figure 1 shows the latest upgrade to the microfading spectrometer. The probe head is re-designed so that it operates in retro-reflection mode hence avoiding the need for alignment between the illumination and collection probes. As a result, the probe head is significantly more robust and compact; measuring only 12 cm by 4 cm. The motorized focusing stage, the X-Y stage, the shutter for the light source and the spectrometer are all computer-controlled by the same program ensuring synchronization of the measurements with the light source shutter and hence improved accuracy in the fading measurements.

Similar to the instrument described by Lerwill et al. (2008), a high-powered continuous-wave xenon light source (Ocean Optics HPX2000) is used with a filter that cuts off the ultraviolet and near infrared radiation. An Ocean Optics HR2000+ portable fibre optics spectrometer is used instead of an Avantes spectrometer. The two brands of spectrometers have similar designs and the choice of the Ocean Optics spectrometer is for compatibility with the Ocean Optics light source in order to synchronize control of the shutter and the spectrometer.

Auto-focussing is achieved by attaching the probe to a computer-controlled motorized linear micrometre stage and finding the position when the counts detected from the reflected light is a maximum. The light intensity is always reduced by an attenuator during focusing. The user is able to monitor the colour and spectral changes online.

Fading rate and degradation rate

It is the convention to measure the light-sensitivity of a material through monitoring the colour change ΔE over the time of exposure, which is useful as an indication of how noticeable the degradation is. However, colour change does not correspond to the rate of degradation linearly and nor does it correspond linearly with the measured spectral reflectance. This paper presents not only the colour change but also the change in spectral reflectance $\Delta R = R(t) - R(0)$ averaged over the wavelength range where the change is occurring. The most perceptually uniform colour space is CIE2000, with colour difference expressed as ΔE_{00} (Luo et al. 2001, Sharma et al. 2005). However, for convenience of calculation, ΔE_{ab} (also called ΔE_{76}) (CIE 1986) and ΔE_{94} (CIE 1995) are still commonly used within the conservation community (Druzik 2010), although they are perceptually less uniform, which means that a ΔE_{76} value might be perceptible for some colour, but not for others. Here the authors will use ΔE_{00} throughout the paper but give comparisons in ΔE_{ab} and ΔE_{94} for fading of common standards like the ISO blue wool series, of which standards BW1, BW2 and BW3 have been used as comparators by earlier (Whitmore et al. 1999) and current microfadometer researchers.

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System accuracy and repeatability

The stability of the system was examined in detail and found to have a systematic drift of ~2% over 60 hours of continuous run. The drift had the greatest rate of change of 0.5% in the first hour of the spectrometer taking measurements. This indicates that the initial drift was partly due to the spectrometer warming up as the steeper slope at the start of taking measurements was observed even after the lamp had been on for a number of hours. It is important to note that the relationship between the observed drift in counts (or reflectance) and colour change ΔE is not linear. In the following sections, the drift in ΔE_{00} is simulated for each material based on their initial spectral reflectance and the observed system drift measured from the light reflected off a stable ceramic white tile.

Accuracy of auto-focus was tested on a standard matt ceramic white tile. The peak intensity has a plateau over a distance of 40 microns around the focus position. The accuracy at finding the focus position is better than 20 microns. Re-focussing on the same spot (i.e. not moving the X-Y stage) using auto-focus gave accuracies of 0.2% in reflectance for the standard matt white tile and 0.06% for a standard matt ceramic black tile.

As with any microfading technique, if the typical roughness scale of the material is of the order of the spot size, then the surface texture would cause variations in spectral reflectance and colour across the surface. Conventional spectrometers and colorimeters have measurement spot diameters of 3 mm to 8 mm, whereas typical spot sizes in microfading are 0.25 mm to 0.5 mm full-width half-maximum (FWHM).

Spot size and efficiency of the system

In order to measure the diffuse reflection from a material, the probe is set up at 45° to the surface of the sample in a retro-reflection geometry. Figure 2 shows a profile of the incident spot across the major and minor axes as measured by a CCD camera. The minor axis of the spot is ~0.46 mm FWHM similar to the original Whitmore et al. design (~0.4mm) but larger than the ~0.25mm in our previous design given in Lerwill et al. (2008). The total power over the focused spot is ~2 mW and the average intensity is ~7 kW m^{-2} over the elliptical spot of 0.46 mm by 0.76 mm. It is ~7 times less in intensity than our previous design (Lerwill et al. 2008), i.e. ~2x10^6 lux, and ~3 times less than the original Whitmore et al. instrument (1999).

Figure 3 shows the change in the mean spectral reflectance ΔR, the rate of change dR/dt of BW2, as well as the colour change corresponding to the evolution of the spectrum averaged over three fading measurements. BW2 was found to reach ΔE_{00} ~0.7 after 20 minutes. The same colour change was reached in 2.5 minutes (Whitmore et al. 1999), 1.5 minutes (Lerwill et al. 2008) and 4 minutes (Druzik 2010) in different instruments.
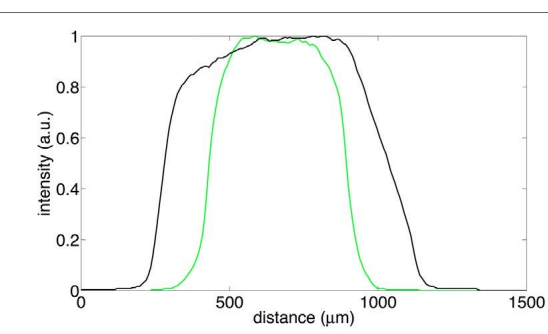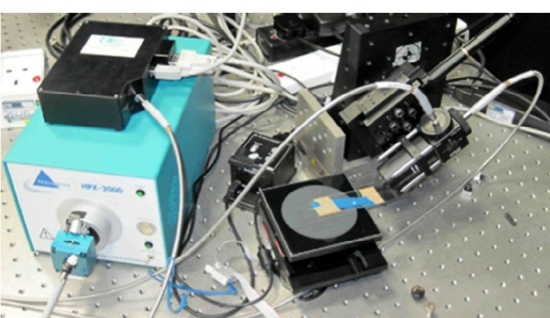

Figure 1
A picture of the upgraded microfading spectrometer showing the light source (blue box), spectrometer (black box above the light source), the probe on the right attached to a motorised linear stage, the input and output fibre optics attached to the probe and a sample placed on a motorised stage

Figure 2
Profiles of the focussed spot along the minor axis (green line) and the major axis (black line)
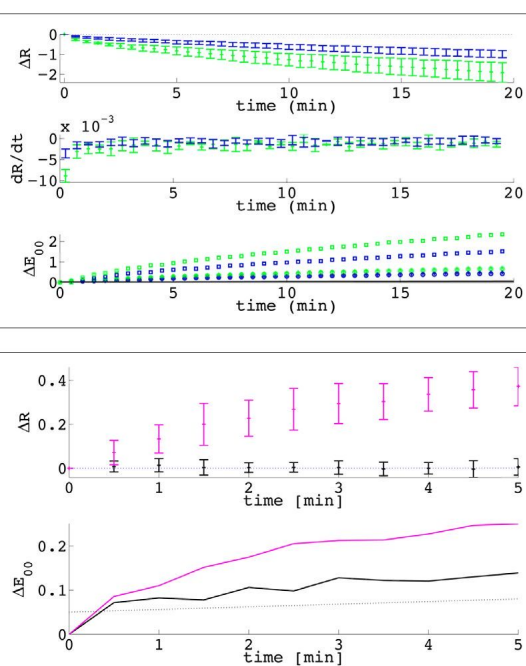
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Being slower means it is less efficient, but by reducing the intensity by almost an order of magnitude means it is more likely to yield realistic results closer to exhibition conditions. Using ΔR or dR/dt plot as a guide, the lightfastness of BW2 can be determined within the first minute when dR/dt is greatest. It is easier to use ΔR than ΔE for the determination of lightfastness of materials, because of the simplicity in the error estimates associated with ΔR. ΔR measures the initial rate of degradation as well as providing a higher signal to noise measure than dR/dt by calculating the accumulated change over time.

The measurement integration time was typically 7ms and the number of spectra averaged was 10. Increasing the number of averages beyond 10 has little effect on the signal-to-noise ratio. For comparison, the rate of change in spectral reflectance due to the initial hour of drift corresponds to 1.4×10^{-4} percent per second and the effect on the colour change due to the drift of the system was found to produce a change of $\Delta E_{00} = 0.06$ for BW2 over the hour.

The large spread in BW2 measurements is due to the surface texture of the wool which was found to be ~ 200 microns in height and 800 microns in the lateral direction (same order as the size of the focused spot) using optical coherence tomography (OCT) (Liang et al. 2005, Spring et al. 2008). The sample was placed between two glass microscope slides in order to reduce the surface texture. The fading was reduced to $\Delta E_{00} \sim 0.4$ after 20 minutes when measured through the 1 mm thick glass microscope slide.

PARAMETERS AFFECTING MICROFADING

The effects of different substrates, thickness of the paint, shade (or concentration of the pigment) and binding medium are examined to understand to what extent these parameters affect the fading rates. Samples were painted out on glass microscope slides, waterleaf paper and filter paper. In the following experiments, samples on paper were clamped between two glass microscope slides to keep them flat. The experiments were conducted in a temperature controlled lab at $\sim 22°C$.

Effect of substrate

The stability of the substrates, waterleaf paper and filter paper, were tested first. The spectral reflectance of the two types of paper is fairly similar with average reflectance of $\sim 67\%$ within the visible range (400-700nm). Figure 4 shows that filter paper is more stable than waterleaf paper.

To examine the effect of substrate on the fading of a pigment, a sample (Tate Gallery Archive 7315.7 TTB6) of Prussian blue from the studio pigments of J.M.W. Turner (1775–1851) was mixed in gum Arabic and painted on waterleaf paper, filter paper and a glass microscope slide. The average spectral reflectance of the paint on filter paper and waterleaf paper were similar at $\sim 14\%$, but the paint on glass placed over a white

Figure 3
Direct fading of BW2 (green symbols) and BW2 clamped between glass microscope slides (blue symbols). Top: evolution of ΔR in the wavelength range of 450nm to 490nm in units of percentage reflectance; the error bars are plus and minus one standard deviation and the dotted line is the system drift. Middle: evolution of dR/dt in the same wavelength range as above (in units of percentage reflectance per second). Bottom: the corresponding evolution of colour difference (circles indicate ΔE_{00}, crosses indicate ΔE_{94}, squares indicate ΔE_{ab}); the black line close to zero is the expected colour change from the system drift in ΔE_{00} units

Figure 4
Fading of waterleaf paper (magenta) and filter paper (black). Top: evolution of ΔR for waterleaf paper averaged over 400-500nm and filter paper averaged over 400-700nm; the dotted line corresponds to the system drift. Bottom: the corresponding colour change; the dotted line show the simulated colour changes due to the system drift

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background was fainter at ~6%. Figure 5 shows that it degrades faster on waterleaf and filter paper than on glass. In all cases, rate of change is greatest at the beginning of the exposure.

Effect of thickness and concentration of paint

The initial average spectral reflectance over the 400 to 700nm range for the two shades of Prussian blue painted in gum Arabic on filter paper range between 9 to 14% and between 35 to 41% for the darker and lighter shades respectively. Figure 6 shows that in this case the fading rate is independent of the concentration of the pigment.
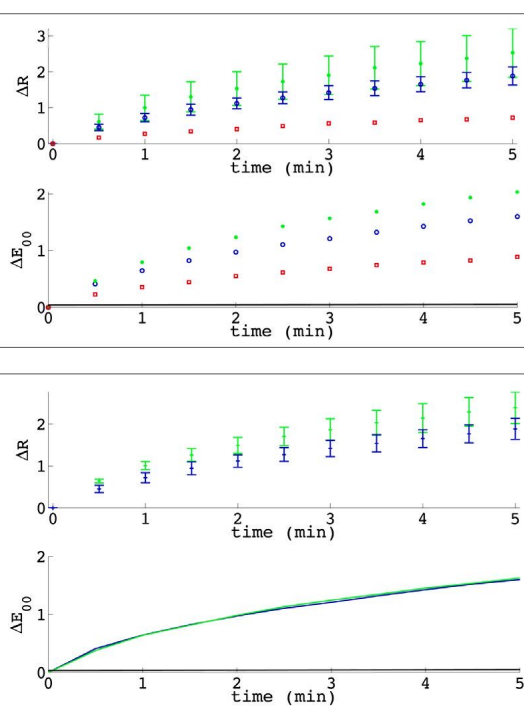
Orpiment mixed in linseed oil and painted on glass microscope slides in varying layer thickness was tested. The OCT measured thicknesses were 400 microns, 320 microns and 100 microns. Figure 7 shows that the fading rate is the same for the two thicker samples but slower for the thinnest sample. The samples were painted out three years ago and kept in dark storage. However, the thinner sample appears to have started to degrade over the years. It was noticed that the same orpiment pigment kept in a glass bottle had started to degrade, since those pigments next to the glass have started to turn orange. The pigment powder pressed between two glass microscope slides was also tested and found to fade differently than those mixed with linseed oil and painted out on glass microscope slides. The thickness of the pigment powder was found to be 400 microns from OCT images. The difference between the final and initial spectra also showed that the thinnest sample and the powder sample responded differently compared to the two thicker samples after the same amount of exposure. Note that the turning point in the reflectance spectrum of the orpiment sample is at ~550nm.

Reciprocity

The validity of accelerated aging methods depends on the reciprocity principle to a large extent. The reciprocity principle states that the amount of degradation only depends on the total energy that the sample is exposed to. Microfading spectrometers usually operate at light intensity levels that are at least 4-5 orders of magnitude greater than exhibition lighting. The intensity of the current instrument is about 4 orders of magnitude more intense than exhibition lighting. Reciprocity principle over 3 orders of magnitude was tested on a 400 micron thick paint of orpiment in linseed oil. Orpiment was chosen because it fades fast and has been tested for reciprocity in conventional accelerated aging experiments using light boxes and found to obey the reciprocity principle for light intensities between 80 and 8000 lux judging by ΔE_{ab} (Saunders and Kirby 1996). Figure 8 shows that reciprocity principle breaks down for the orpiment sample where the reaction pathway is different for the different light intensities. The degradation appears to be slowed down for intensity levels between 2×10^4 and 2×10^5 lux. It should be noted that the orpiment sample used here and the one used in Saunders and

Figure 5

Top: evolution of ΔR (averaged over the wavelength range of 440nm to 480nm) of TTB6 (Prussian blue) in gum Arabic on glass (red), filter paper (blue) and waterleaf paper (green). Bottom: the corresponding colour change; the expected effect due to the system drift is shown as a black line

Figure 6

A sample of TTB6 in gum Arabic painted in two shades on filter paper (the blue line shows the darker shade and the green line shows the lighter shade). Top: ΔR (averaged between 440nm and 480nm) in units of percentage reflectance. Bottom: corresponding colour change; the expected effect on colour change due to the system drift is shown in solid black

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Kirby (1996) are from different manufacturers. Tests of Prussian blue also showed that reciprocity breaks down.

CONCLUSIONS

The advantage of the latest upgrade to the microfading spectrometer is the automation such that all parts of the instrument are centrally controlled by a laptop and that the probe is more robust, smaller in size and easy to use with no need for alignment. These improvements increase the portability and user-friendliness which can potentially increase the use of microfading tests to assist conservation management decisions.

The evolution of the change in average spectral reflectance ΔR over a spectral region where most of the change occurs can be used as an alternative to monitoring degradation rate through colour change. It is easier to understand the statistical characteristics of ΔR than ΔE. Since degradation of material is independent of human vision, there is no real advantage in monitoring ΔE other than noting the visibility of the damage.

The reciprocity principle was tested on an orpiment sample and found to break down. Since reciprocity is most likely to break down at the highest intensities typical for microfading, it is both efficient and important to examine reciprocity at the top one or two orders of magnitudes in intensity for a significant sample of common pigments in the future. It is likely that many pigments do not follow the reciprocity principle at these high intensities, but microfading is still likely to provide a prediction for light induced degradation that results in conservative decisions for light exposure.

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Figure 7
Fading of orpiment in linseed oil at various thickness (400µm in black, 320µm in green and 100µm in blue) and a 400µm layer orpiment powder packed between two glass microscope slides (in red). Top: evolution of ΔR averaged between 520 and 545nm. Middle: colour change. Bottom: difference spectra between the final spectrum and the initial spectrum

Figure 8
Reciprocity test on a 400µm thick layer of orpiment in linseed oil paint on a glass substrate using 100% (black line), 10% (green line), 1% (blue line) and 0.1% (red line) of the total intensity (~2x10⁶ lux). Top: ΔR between 520 and 545nm in units of percentage reflectance as a function of incident energy; note that 80mJ is equivalent to ~2x10⁴lux·h. Middle: colour change as a function of total energy of exposure; the dotted lines correspond to simulated effects due to system drift for fading periods associated with each intensity levels. Bottom: difference spectra after a dose of 55mJ and the initial spectrum

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