A PORTABLE MICRO-FADING SPECTROMETER FOR VERSATILE LIGHTFASTNESS TESTING

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The design and experimental method for the use of a novel instrument for lightfastness measurements on an artwork is presented. The new micro-fading spectrometer design offers increased structural stability (which enables portability) and increased versatility over the previous, published design, broadening the scope of locations at which data can be acquired. This reduces the need for art handling or transportation in order to gain evidence-based risk assessments for the display of light-sensitive artworks. The instrument focuses a stabilized high powered xenon lamp to a spot 0.25 mm diameter (FWHM) while simultaneously monitoring colour and spectral change. This makes it possible to identify pigments and determine the lightfastness of materials effectively and non-destructively. With 2.59 mW or 0.82 lumen (1.7 \cdot 10^7 lux for a 0.25 mm focused spot) the instrument is capable of fading Blue Wool 1 to a measured 11 \Delta E_{ab} value (using CIE standard illuminant D65) in 15 min. The temperature increase created by focused radiation was measured to be 3 to 4 °C above room temperature. The system was stable within 0.12 \Delta E_{ab} over 1 h and 0.31 \Delta E_{ab} over 7 h. A safety evaluation of the technique is discussed which concludes that some caution should be employed when fading smooth, uniform areas of artworks. The instrument can also incorporate a linear variable filter. This enables the researcher to identify the active wavebands that cause certain degradation reactions and determine the degree of wavelength dependence of fading. Some preliminary results of fading experiments on Prussian blue samples from the studio materials of J. M. W Turner (1755-1851) are presented.

1 Introduction

Those responsible for the world’s cultural treasures within museums have a duty to preserve these works whilst allowing public access. Often these two requirements result in museum policy being driven in opposing directions. The necessity of illumination for the display of
photo-sensitive works of art is an example of this impasse. Therefore, the application of technology to solve issues in the conservation and display of works of art warrants further investigation.

To determine the safety of display and effectiveness of display policy, a novel micro-fading spectrometer has been designed and constructed taking inspiration from the Whitmore design\textsuperscript{1,2} and its application\textsuperscript{3,4,5}. An instrument was constructed that was capable of identifying materials more light sensitive than Blue Wool #2 through direct fading in artworks on a sub-millimetre diameter spot such that the faded spot is not discernable by the viewer. Fading and colour change are carried out simultaneously.

It is intended that some improvements on this design will increase the portability and ease with which a researcher can conduct micro-fading, so the need for object transportation is reduced, and therefore the rate and also scope of locations at which data can be acquired increased.

To increase the accuracy of colour measurements and improve the ease of application, some changes to the previous design were implemented. An improvement of the precision of probe positioning relative to the sample, a good homogeneity of illumination across the faded area, a controlled intensity at the illuminated surface from the lamp, and an improved ease of confocal probe alignment were amongst the changes. A reduction in the heating of the sample area by the illuminating spot was also achieved and a method of documenting the exact location of fading on an artwork is being developed.

The instrument also differs from a previous design by Paul Whitmore \textit{et al} in that a linear variable filter system was added, which enables assessment of the wavelength dependence of fading and broadens the scope of information that can be acquired regarding fading of artist’s materials.

Tests are carried out on sub-millimetre diameter spot size while at the same time monitoring change in the reflectance factor of the sampled region. To do this the monitored spectrum is converted using the Commission International de l’Eclairage (CIE) 1976 \textit{L*a*b*} equation for the 2° standard observer under the standard illuminant D65. Via this method an automated calculation of colour difference of the fading spot is monitored in real time in \(\Delta E_{ab}\) units.

2 Instrument Design and Performance

2.1 Instrument Design

The instrument developed is approximately half the cost of the previous published design. It is a flexible, compact, lightweight and mobile instrument which removes the need for transportation of art work and unnecessary art handling (Figures 1 and 2). It can function in two modes of operation: firstly, as a transportable compact microfading spectrometer capable of identifying the sensitivity of artifacts to visible light exposure, and secondly, with a linear variable filter to increase the scope of investigation beyond that of the broad spectrum. The latter application is discussed further in section 3.

For use as a microfadometer, a high-powered continuous-wave xenon light source (Ocean Optics HPX2000) is connected directly to a solarization resistant optical fibre with a 600 micron fibre core. The end of this fibre is connected to a confocal probe designed for this task, containing two matched achromatic pairs. Light passes through an extended hot mirror utilized to remove the infrared in order to reduce temperature and the ultraviolet to better simulate the museum environment (Figure 3). The filtered light is focused to a 0.25 mm spot by the matched achromatic doublet pair on the sample surface.

It is possible to move the location of the lenses in the probe as they are contained within lens tubes on adjustable mounts. Adjusting the position of the first lens (from the light source) alters the working distance and the size of the focused spot size. To a certain extent it is possible to do this without significantly altering the fading rate. This is because moving the first lens closer to the fibre output couples more light to the spot which compensates for the increase in fading area. This possible alteration of the instrument can lead to increased sampling area, and therefore data that is more representative of varied and highly-textured surfaces. This would be useful for example when fading reconstructed paint samples rather than actual art work where a small faded area is not an important safety measure to prevent visible damage.

In order to monitor colour change, scattered light from the small sample area is then coupled back into the optical system via another optical probe of the same design at 45 degrees to the normal. Sampled radiation then passes through a neutral density filter to avoid saturation of the fibre optic spectrometer. The spectrometer (Avantes Avaspec 2048) receives this signal via an optical fibre, and
the software (AvaSoft 7.0) analyzes change in the spectrum and the rate of fading occurring in real time.

The probe is mounted on an XYZ stage capable of sub-micron scale movements. The Z axis stage is motorized. It is therefore possible to achieve fine alignment of the probe with the surface remotely rather than leaning over the artwork. This in turn enables adjustment when the probe is beyond arms-reach, e.g. over an art work when the probe is mounted on a gantry to enable movement over the surface of an artwork that is laid flat. This is also an important aspect of the design, as it becomes possible to achieve best focus remotely.

To achieve best focus, the software gives the integrated counts from the reflected spectrum over the full spectral range (400 to 700nm), which enables fine adjustments undetectable when aligning by eye. By making small incremental adjustments in position that would not be possible using a manual micrometer screw, it is possible to define best focus to a greater accuracy.

Future efforts to develop the instrument will include attaching a webcam to the probe which will enable a record of the location of fading on an artwork to be recorded. As well as this, an automated
fadometer system is in development which will be used to produce large amounts of data for a variety of samples and enable greater throughput to more accurately categorize the behaviour of a larger number of samples.

2.2 Probe Alignment

To ensure confocality, both probes were illuminated with low intensity radiation and focused onto a CCD chip (Figure 4). For easier analysis, in Figure 4c the red area indicates the sampling area of the receiving probe and green the illuminating area (this creates a yellow overlap). The yellow region indicates where both fading and colour monitoring takes place.

When correctly aligned, it was shown that best focus of the probe provides the maximum signal to the spectrometer, and ensures reproducible spot size. Failure to align correctly leads to the probe focusing incorrectly, which can lead to a large variation in the calculated fading rate.

To fade a sample, the instrument operates as a reflectance spectrometer with a high powered light source. In order to make reflection measurements, a dark spectrum and reference spectrum are acquired. The reference spectrum is recorded on a polished barium sulphate sample. A neutral density filter is used to reduce the beam to a level where best focus can be obtained without a significant level of radiation being incident on the sample. The probe is adjusted on the sample in order to come to best focus and acquire maximum reflected intensity on the object in the desired location. The shutter of the lamp is then used to stop illumination as the neutral density filter is being taken out in preparation for fading. Colour differences are monitored in real time using the spectrometer software in order to prevent fading beyond acceptable levels which have been independently determined in the development process.

2.3 Light Source Behaviour

The instrument produces 2.59 mW or 0.82 lumen (1.7·10⁷ lux for a 0.25 mm focused spot). The relative power spectrum of light incident on the sample measured using a calibrated spectrometer is shown in Figure 5. The xenon bulb output will alter as it ages and this makes it necessary to monitor probe output regularly.

If it is desired to compare the time a sample undergoes fading using the fadometer to years in a gallery setting, we need to assume the sample would fade to the same degree independent of the rate in which it is faded (or that reciprocity holds). At 50 lux for 8 h per day 7 days per week, the fading rate of the instrument can be considered as 1 min approximately being equivalent to 2 years in a gallery setting assuming reciprocity holds over 5 orders of magnitude. We will examine the issue of reciprocity for a range of fugitive pigments in a separate study. Unlike conventional fading, the microfadometer is capable of testing reciprocity over at least 4 orders of magnitude. Other limitations of the technique which prevent more certain statements in this vein being made, such as difference in the spectral power distribution between gallery lighting and the xenon lamp of the instrument and sample colour reversion are discussed by Whitmore et al.
Analysis of the stability of the system took place over 400 min using illumination of barium sulphate as a non fugitive reference over this period. Variation at any wavelength from 410 to 720 nm was within 1.5% with the majority within 1% variation.

Total counts of the spectrometer at all wavelengths increased 1.1% over the period (Figure 6). The dark current over 7 h was constantly monitored and subtracted by the spectrometer software.

The stability of the system was shown to produce an error no greater than ΔE_ab of 0.31 at any reading over the 7 h period. The initial hour produced no more than a ΔE_ab of 0.12 at any reading.

2.4 Probe Position Sensitivity

In order to determine empirically the diameter of the area that would be faded by the incident light, the focused spot of the probe was analyzed by observing its alteration through focus using a CCD. FWHM values were taken when varying the working distance of the probe to the CCD (Figure 7) which gave a spot size on the CCD chip of 33 pixels or 0.25 mm. It was verified that 1 pixel width was 7.5 µm as per manufacturer specifications. From this technique it was possible to determine the spot size diameter to 1 pixel or 6% of the fading area. Figure 7 illustrates that the diameter of the spot did not alter for 50 µm through focus.

The effect that small errors in focusing have on received signal and colour measurements was investigated. The sensitivity in positioning of the probe relative to the surface being sampled was determined by calculating relative ΔE_ab at various locations through focus, compared to values L=100 a=0 b=0. This provided an illustration of how a small change in probe position, (for example relaxation of the probe holder, or altering of the sample/probe geometry in repositioning the probe from the white target to sample) can create error in measured colour.

The relative colour difference was measured moving the probe in 50 nm increments through focus along the optical axis when illuminating a polished barium sulphate white tile. Colour data readings are shown in Figure 8, demonstrating that the colour measurements did not alter for 40 µm through focus. From this analysis, colour measurement is shown to be more sensitive than the variation in size of the illuminated spot with probe position, as it is required not only that the spot be focused but also the two probes be aligned.

In order to investigate the accuracy of colour measurement using the instrument, reflectance standards were used to investigate the accuracy of the instrument in comparison to results from other colour measurement techniques. This indicated that some standards, although accurate and reliable for use with colour measurement instrumentation that use relatively large sampling areas, these standards are less accurate on the scale of measurement of the instrument under discussion (0.25 mm). It was found a significant variation in reflectance over the surface can be observed over the sub-millimetre scale for all reflectance standards.

2.5 Sample Visibilty and Size

A series of faded spots were produced ranging from ΔE_ab 1 to ΔE_ab 8 on both Lightcheck ULTRA and Lightcheck Sensitive (Figure 9). Lightcheck is made of a light sensitive coating printed onto a paper substrate. The colour changes of Lightcheck indicate the degree of exposure. These samples were chosen as they provide an approximation to a worst case scenario in that they both provided very smooth highly fugitive surfaces. With both types of sample, it was possible to observe many
spots in the series. It was found that 5 different
observers if shown the location could see spots
down to a colour difference of 2 or 3 ΔE_ab units on
a pristine Lightcheck surface under good lighting.
Importantly it was found that in situations where
the Lightcheck surface was altered to reduce uni-
formity, for example by folding to vary the surface
texture, it was impossible to see to such low levels
of damage.

Practically speaking, when fading rougher, more
textured, varied surfaces, for example when fading
samples of oil paint on canvas it is possible at
times to fade to ΔE_ab of 15 and more and not
observe any alteration as has been previously
considered the case.1 This indicates that the dam-
age is hidden by the texture in which it exists and
can be visible even at such low levels of fading.

These findings are further verified when fading
watercolours. It is possible at times to fade to ΔE_ab
15 and beyond and observe no change visually.
However this depends on the uniformity of the sur-
face. Importantly, on many samples which were
very uniform, such as various Prussian blue sam-
ples a fade of 5 to 6 ΔE_ab was visible on close
inspection and often also at reading distance (25
cm).

After fading the series it was possible to image the
damage profile of each spot. An image of a spot
faded to a colour difference of 5 ΔE_ab on
Lightcheck Sensitive was captured using a cali-
brated microscope. Analysis showed good uniform-
ity of illumination and fading across the focal
region. As well as this, a typical example of the
measured normalized profile of a 5 ΔE_ab faded
spot, and a measured normalized profile of the incident illumination at best focus was also com-
pared and shown to match well (Figure 10). The
microscope camera was calibrated to 800 pixels
per mm and this showed a variation in the FWHM
spot size dependent on the degree to which we
faded. This ranged from 0.22 for ΔE_ab of 2 to 0.25
for ΔE_ab of 8. A separate investigation of spot size
up to 16 ΔE_ab showed that continued fading led to
continued increase of FWHM spot size.

3 Wavelength Tunable System
3.1 Technique Introduction

Colourants that are regarded as fugitive are faded
predominantly by the visible region,7 therefore the
effect of visible radiation of different wavelengths
on deterioration of fugitive pigments warrants fur-
ther investigation via a wavelength tunable sys-

It is possible to filter the xenon lamp of the instru-
ment using linear variable filters (Ocean Optics
LVF-UV-HL and LVF-HL) to move through the
desired wavelength range, and shape the fading
spectrum. The filter bandwidth of this technique is
20 to 30 nm FWHM and it is possible to vary the
central wavelength of the filter in the visible range
(Figure 11)

In previous efforts to investigate the wavelength
dependence of fading, Aydinli, Krochmann et al.8
and McLaren7 divided the visible spectrum into 3
wavelength sections to observe the relative
degree of damage. In later work by Kenjo,9,10 the
number of divisions increased to seven wave-
bands (located from 390 nm to 700 nm) on six dif-
ferent colorants. Similarly, Saunders and Kirby11
used broad band interference filters with band-
widths of 70 nm, peak transmittances at 50 nm
intervals in the visible range from 400 nm to 700
nm.

Building on this work and utilizing new apparatus,
the wavelength dependence of fading of many pig-
m ents and samples can be investigated further
and at a greater resolution than previously
attempted. This will be done to highlight active
wavebands and determining the wavelength speci-
ficity of degradation caused by the specific visible regions for light sensitive materials.

### 3.2 Experimental Method

The tunable instrument operates in a similar way to that described previously. The spectra must be recorded before and after fading in order to obtain a colour difference value.

After an initial reading has been taken, the variable filter is adjusted to the chosen wavelength prior to fading the sample. The filter is then removed after fading to take a spectral measurement. Due to the presence of the filter, colour measurements are not possible during fading unless the shutter is opened, the filter removed, and a measurement rapidly taken in order not to alter the degree of fading.

In order to gain information on the wavelength dependence of fading, the variation in power with wavelength of the instrument must be compensated for. This is because neither the transmission of the filter system (Figure 11), nor the power of the
xenon source at various wavelengths is constant (Figure 5).

The addition of the variable filter holder increased the distance between the light source and the fiber, thus reducing the incident power to 1.46 mW or 0.46 lumen at focus (without the variable filter). This reduction in incident power leads to a reduction in fade rate.

It was found that fading spot size remains at 0.25mm when sampled using a CCD at intervals from 400 nm to 700 nm using the same technique as discussed in section 2.4.

The technique of initially monitoring the sample lightfastness using a broad spectral fade enables the user to determine a suitable length of time to fade the sample. A half hour period has typically been used to fade samples as fugitive as Blue Wool 1 to 2. Results from this technique are presented in section 4.3.4.

4 Results and Discussion

4.1 Rate of Fading

ISO Blue Wool Standards are an internationally accepted method of measuring fading within the conservation community. Eight different degrees of lightfast dyes can be used (with 1 being the least lightfast to 8 the most). The effect of fading Blue Wool samples 1, 2, and 3 by focusing 2.59 mW to a 0.25 mm diameter area can be seen in Figure 12. This illustrates that the instrument is capable of fading Blue Wool 1 to a ΔEab value of 7 in just over 5 min and Blue Wool 2 to the same level in twice that time period as expected.

4.2 Temperature Increase

In order to evaluate the safety of the instrument for use on artworks and to know to what degree temperature may play a part in any observed results, it was necessary to quantify the temperature increase caused by the focused radiation. Two techniques were employed. On separate occasions two different thermocouples were coated...
with various light and dark paint samples on paper and illuminated by the focused spot. A thermocouple was also lightly coated with a variety of paints as well as exposing the bare sensing junction.

The same temperature increase of 3 °C to 4 °C above room temperature was observed in all cases.

As a second method, a thermometer that contains heat-sensitive (thermochromic) liquid crystals that change colour to indicate different temperatures was used. A number in a series corresponding to the environmental temperature becomes translucent when it is reached. By focusing the probe onto the various temperature-sensitive numbers, 26 °C clearly altered whereas all others from 12 to 34 (increments of 2 °C) did not. The area heated by the radiation remained briefly unaltered after the light was removed by a shutter, before cooling. A photograph of this can be seen in Figure 13.

4.3 Application to Prussian Blue Pigment

One pigment has consistently been reported to be phototropic (that is, to lose colour due to light exposure, and to regain it in the dark): Prussian blue, ferric ferrocyanide, iron(III)hexacyanoferrate(II), conventionally represented as Fe₄[Fe(CN)₆]₃·xH₂O. The formula quoted by Berrie is more correct: MFe³⁺Fe²⁺(CN)₆·nH₂O, where M is a potassium (K⁺), ammonium (NH₄⁺) or sodium (Na⁺) ion, and n=14-16. Reports of fading in light in the presence of normal air and/or nitrogen have been summarised by Kirby and Rowe. Complete colour loss under hydrogen was noted by Russell and Abney. Reduction of Fe(III) to Fe(II), a reversible reaction, is the cause of this reversion.

4.3.1 The Effect of Water Dilution

The effect of water dilution of the Prussian blue sample in gum Arabic medium was investigated. Painted samples on filter paper were prepared from an undiluted stock suspension of Prussian blue in gum Arabic (Neat), 1 part Prussian blue sample with gum Arabic to 1 part water (1 to 1) and 1 part Prussian blue sample with gum Arabic to 5 parts water (5 to 1) in various dilutions through to 1 part Prussian blue sample with gum Arabic to 100 parts water (1 to 100). The results of the rate of fading can be seen in figure 14. Fading rate is dependent on the intensity of the colour wash: a very dilute wash does not cover all of the paper substrate with pigment particles, and as the pigment is the most light sensitive component, increasingly pigment-rich samples fade more rapidly.

4.3.2 The Reversion of Colour

Colour reversion of Prussian blue samples in the dark was also investigated over a period of 2 days with 2 colour reversion periods. The sample was fixed in position and then faded. During the 2 reversion periods (14 and later 10 h) the sample was kept in darkness by housing it to remove incidental light. The probe was not moved during the experiment. Colour measurements during the fading process along with changes due to reversion are represented in Figure 15.

The pigment became less sensitive to the exposure of light after the initial cycle of fading. Further investigation is necessary to establish how long (or if at all) it takes for the reversion in the dark to bring back to its original value. As previously stated a reversible reaction between Fe(III) to Fe(II) is the cause of this reversion.

4.3.4 The Wavelength Dependence of Fading

The degree of fading by filtered radiation from 400 nm to 700 nm (bandwidth 20-30 nm FWHM) was investigated in increments of 25 nm through the visible region for a neat Prussian blue sample. The length of time with which which we faded was altered at
each wavelength. This was done in order to compensate for the variation in incident power with wavelength caused by the spectral power distribution of the lamp (Figure 5) and varying transmission of the filter at each wavelength (Figure 11). This resulted in a power distribution at focus as illustrated below in Figure 16.

With the linear variable filter in place, the temperature was measured by the thermocouple, and was found to increase by approximately 1 °C independent of wavelength.

Figure 17 shows a preliminary result of the action spectrum of the Prussian blue tested, that is colour change as a function of wavelength for the same amount of incident energy at each wavelength. The action spectrum shows that the blue end of the spectrum causes more damage than the red part of the spectrum. Further results of this type applied to other samples will be presented and discussed in a future publication.

5 Conclusions

A novel instrument and a new experimental method have been presented and employed that enables the investigation of photosensitive samples and works of art. The instrument demon-
strates increased structural stability increasing the portability over an earlier design, broadening the scope of locations at which data can be acquired.

Increased precision of probe positioning relative to the sample, homogeneity of illumination across the faded area, controlled intensity at the illuminated surface from the lamp, and an ease of confocal probe alignment are present in the new design.

Two different measurement methods indicate a temperature increase of 3 to 4 degrees during fading experiments.

The instrument is capable of fading Blue Wool 1 to a ΔE\text{ab} value of 7 in just over 5 min and Blue Wool 2 to the same level in just over 10 min.

Incorporating a linear variable filter enables the investigation of the wavelength dependence of fading of many samples to a greater resolution than previously attempted.

It was also found that colour change is not the only factor that increases the visibility of faded spots. The smoothness and uniformity of a surface also plays a role, leading to the conclusion that damage is hidden by the texture of its surroundings. When fading very smooth and uniform surfaces colour change was observable in the case of very small differences. Therefore under certain circumstances, greater caution should be employed when the prevention of visible bleaching is a consideration of the fading process.

Investigation of the error in colour measurement, and colour difference calculations produced by small differences in position, indicated that alignment by eye may be a significant cause of error in measurements. A motorized micrometer stage used for fine adjustment of the focus can reduce the errors.

Suitable future efforts will be in creating an automated focusing method which would be more suitable for increased accuracy and repeatability of measurements. Following this, improvements to create full automation of the instrument will take place in order to characterize a large number of samples many times without human intervention. In doing so, it will be possible to gain large amounts of data for single samples, and therefore errors due to such small sampling area can be reduced by averaging over a very large number of fades when investigating samples rather than real art works. Larger sample sets and increased spot size are also desirable in order to increase the reliability of future wavelength dependent investigations.

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7 References


