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Journal:	<i>LEUKOS</i>
Manuscript ID	LEUK-2018-0025.R2
Manuscript Type:	Scientific Research Results
Manuscript Keywords:	Colorimetry, LED Sources and Systems, Fourier-transform infrared spectroscopy, Multivariate Analysis, Historic House

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ASSESSING THE IMPACT OF LED LIGHTING ON THE STABILITY OF SELECTED YELLOW PAINT FORMULATIONS

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ABSTRACT

Light Emitting Diodes (LEDs) are steadily finding application in an increasing number of museums and heritage institutions, providing energy efficient solutions for collections display. Although there is a business case to be made for moving towards LED lighting the safe display of objects must also be ensured. Identifying vulnerable pigments and paints ensures future preservation strategies to be put in place, avoiding acerbation of damage and reducing the need for conservation. In the first part of our research we investigate color shift and molecular alterations in three yellow paints, namely lead chromate sulfate, arsenic sulfide and cadmium sulfide in linseed oil and gum Arabic binders. Following an artificial ageing regime, color shift was evaluated using colorimetry and molecular alterations were monitored using Attenuated Total Reflectance Fourier-transform Infrared Spectroscopy coupled with multivariate analysis. Up to 80 Mlux h the lead chromate samples in linseed oil displayed equivalent color shift approximating $10 \Delta E_{00}$ on exposure to the three artificial ageing regimes. Color shift has been attributed to the formation of lead oxides evidenced by the appearance of a mid-infrared spectral band at 470 cm^{-1} assigned to PbO_2 . Above 80 Mlux h the formation of lead oxides was exacerbated by exposure to one particular LED. Arsenic sulphide in linseed oil displayed color shifts intensified by both types of LED. Above 40 Mlux h there was a discernible color shift in all samples, with the two LEDs displaying ΔE_{00} values two times higher than those displayed by the tungsten halogen samples. The alterations have been attributed to the formation of As_2O_3 , which is known to form in the presence of wavelengths shorter than 428 nm. Cadmium sulphides in both linseed oil and gum Arabic paints did not display discernible color shift or the presence of degradation products.

KEYWORDS

Colorimetry; LED Sources and Systems; Fourier-transform Infrared Spectroscopy; Multivariate Analysis; Historic House

1. INTRODUCTION

Solid-state lighting systems, commonly known as Light Emitting Diodes (LED), are steadily finding application in an increasing number of museums and heritage institutions, providing energy efficient solutions for collection display. Spurred on by the increased risk of obsolescence of tungsten halogen lamps, and the large outlay of money required for the migration of English Heritage's current lighting systems, our research is directed towards assessing whether particular pigments and binder compositions are vulnerable to chemical alterations, enhanced fading and discolouration when subject to different solid-state lighting environments.

Lighting is a key component in the overall energy performance assessment of a historic building (de Santoli 2015). In 2014, LEDs were estimated to consume one-sixth the energy of incandescent sources, and one-third compared to compact fluorescent sources, and this was expected to improve further as LED technology matures (Solais 2014). The long life of LED illuminants, and consequent less frequent replacement (compared to tungsten) has two main benefits: it minimises physical risk to artefacts from ladders and platforms (Druzik and Michalski 2012); it reduces maintenance costs, which can be especially costly in the vicinity of high-value display items (Thorseth and others 2012). LED lighting systems operate at much lower temperatures than traditional incandescent lamps. As such, the energy required for cooling systems designed to counter the heat generated from incandescent light sources is much reduced, and it has been stated that for every three Watts of power saved when moving to LEDs a further one Watt is saved from the cost of environmental control (Druzik and Michalski 2012).

The research presented here aligns with English Heritage's policy for *Climate Change and the Historic House* (Heritage 2012) through studying the impact of different options for climate change mitigation and adaptation. Through the investigation of energy efficient lighting alternatives for the historic house environment a significant contribution can be made towards national and international targets for climate change (DECC 2012; DTI 2007). Based on estimated annual reductions in energy costs per equivalent lamp, moving from tungsten lighting to LED lighting could theoretically establish an energy and monetary saving in the region of 85%, to be offset against the cost per unit of replacement. However, the aged electrical systems within historic houses, coupled with the limitations on controlling temperatures, will reduce the expected operational life of the lamps. Additionally, many historic interiors have much lower artificial lighting density than museums and galleries, therefore total potential savings may prove less significant than previously reported (Arkinson 2011; ARUP 2010; Druzik and Michalski 2012). Nonetheless a move to LED lighting could prove financially beneficial, coupled with a significant reduction in CO₂ emissions. Although there is a business case to be made for moving towards LED lighting within English Heritage properties, the safe display of objects must also be ensured. Identifying vulnerable pigments and paints will enable future preservation strategies to be put in place, avoiding acerbation of damage and reducing the need for conservation.

With LED for collection lighting still in its infancy there can be large differences in properties between lighting systems, which may pose problem for collections management and display (Druzik and Michalski 2012). One of the major concerns regarding the move from tungsten lighting to LEDs relates to the spectral power distribution output of phosphor-coated short-wave chip LEDs, with some lamps emitting a significant intensity of radiation at wavelengths nearing the ultraviolet region of the spectrum. For museum and gallery applications, white LEDs containing violet chips are not deemed appropriate as these have an intense emission peak at 405 nm, close to the demarcation of UV radiation (Druzik and Michalski 2012; Padfield 2014). Therefore, blue chip LEDs are favoured for museum and gallery applications. This is due to their primary emission being centred at approximately 450 nm and concomitant broad phosphorescent emissions at longer wavelengths (Druzik and Michalski 2012; Padfield 2014; Padfield and others 2013). Although the intensity of short wavelength emissions (405 nm) are greatly reduced when compared to violet chip LEDs, the presence

of emission peaks in the 450 nm region may still be damaging. In a recent survey on museum lighting selection (Garside and others 2017) it was suggested that the peak at 450 nm should not exceed three times the height of the broad phosphorescent emission. Current U.S Government guidelines for the display of works of art suggest that the peak at 450 nm should not exceed 50% of the maximum power in the spectral power distribution (Miller and Druzik 2012).

It is acknowledged that historic house environments routinely display works under UV-filtered daylight conditions, with relative spectral power distribution below the 500 nm region being higher than in blue chip LEDs. However, photosensitive objects are restricted to locations where daylight penetration factors often approach zero. In such cases local lighting often relies on tungsten to illuminate such objects. The output of tungsten bulbs is concentrated at the lower frequency, red end of the spectral distribution. Although dyes and photographs have been assessed and are not adversely affected by exposure to blue chip LEDs when compared to tungsten, previous work indicates certain pigments might be at risk (Lerwill and others 2014; Lerwill and others 2015). Assessing material stability is generally based on reflectance spectra exhibiting weak absorption around the 450 nm region, however this does not definitively indicate stability.

The work presented here is derived from a larger research project aimed at assessing the impact of blue chip LED lighting on the stability of a number of artists' pigments and paints. The project comprised a twelve month light ageing study, exposing a range of paint samples to five lighting environments, namely: UV filtered natural daylight; tungsten halogen; two LEDs; and darkness (control samples). Samples were periodically analysed using Fourier-transform infrared spectroscopy and colorimetry, providing information on molecular alterations and color shift, respectively. Owing to the large dataset (total of 1,620 samples) this project employed a multivariate analytical (MVA) approach, such as partial least squares (PLS). MVA was used to highlight molecular changes in the pigments and paints, and to establish whether structural modifications were associated with color shift, exposure and exposure type.

In this paper we specifically report on three yellow pigmented linseed oil and watercolor paint formulations, namely lead chrome sulfate (chrome yellow), arsenic sulfide (orpiment) and cadmium sulfide (cadmium yellow). The oil paint and watercolor samples were prepared according to recipes reported in original treaties and accounts (Masschelein-Kleiner 1995) and are outlined in the Section 2.2. These samples were exposed to accelerated ageing regimes following a nine month drying period.

2. METHODOLOGY

English Heritage defined the collection of interest as broadly Old Masters (oil paints) and British watercolors from the eighteenth century onwards. References detailing the palette of artists belonging to these groups were sought (e.g. (Kirby and others 1996; Ormsby and others 2005; Townsend 1993b; Townsend 1994a)). The references were assembled and prioritised, which generated a preliminary list of 100 pigments. To narrow down the list of pigments, it was decided to examine pigments which were mentioned in at least two light deterioration experiments *and* at least two palette reviews and had a reflectance spectra indicating potential sensitivity to bluer light (Kirby and others 1996), meaning the pigment was thought to be light sensitive *and* was typically used in the types of work of interest. Consequently some pigments with reflectance spectra of potential interest were discounted due to their relative rarity on the palette. For example, zinc yellow [$K_2O \cdot 4ZnCrO_4 \cdot H_2O$] has an absorption peak at 585 nm, which has been shown to change during ageing (Casadio and others 2008). However, Kuhn and Curran report that its use was not widespread and chrome yellow was more commonly used (Feller 1986).

Although our broader research project encompassed twelve different pigments (Supplementary Information 1) and three paint binding media, here we present the results relating only to selected yellow watercolor and oil paints, namely lead chrome sulfate (chrome yellow), arsenic sulfide (orpiment) and

cadmium sulfide (cadmium yellow). Further results from the broader project will be published in due course.

2.1 LIGHT EXPOSURE CHAMBERS

Accelerated ageing was undertaken using purpose-built light boxes designed and manufactured by Complete Lighting Systems. Accelerated exposure provides insight into the long-term performance of different lighting regimes, within a short time period. Given the sector's misgivings about LEDs, the aim of this project was to establish the extent that paint stability differs on exposure to LED lighting relative to the tungsten lighting, which is currently employed within English Heritage historic house environments. Current English Heritage guidelines restrict the use of LEDs with a 450 nm emission greater than 33% of the broad phosphoresce and with a full width at half height greater than 20 nm. Two LED lighting systems were therefore selected to interrogate the importance of these guidelines. These were compared against an accelerated tungsten lighting regime and a dark control environment. The color metrics for each light source (Table 1) and normalised spectral power distributions (Fig. 1) were measured using a GL Optic Spectis Touch 5.0 *in situ* within each chamber. Where applicable the UV-filters were in place during measurement.

Lighting Condition	Light Source	CCT (K)	Duv	CRI	TM-30 (Rf)	TM-30 (Rg)	%Relative Energy (% of DL)*
D	Dark - Control						
TH	UV filtered dichroic halogen 35 watt 24°	3008	0.0015	94	98	99	65.0
LED1	LED	2997	-0.003	88	96	101	60.5
LED2	LED	3990	0.0013	82	82	100	72.9
DL	UV filtered daylight	5595	0.0058	99	97	99	100

Table 1 Color metrics for the four light sources

* Padfield J. Measuring and Working with Different Light Sources with The National Gallery [Internet]. London: The National Gallery. Available from: <http://research.ng-london.org.uk/scientific/spd/>

Fig. 1 Spectral powder distribution of UV-filtered dichroic halogen lamp (TH), LED1, LED2 and UV-filtered Daylight, scaled to the human phototropic sensitivity function (Padfield 2014)

A further set of samples were exposed in real time to daylight to establish the relative color shift. Samples were exposed to UV filtered daylight and periodically analysed using colorimetry (Fig. 1 and Table 2). Total exposure levels were dependant on seasonal weather conditions, but exposures reaching 5.4 Mlux h were achieved over the duration of the experiment.

Lighting Condition	Sample Nomenclature	Days	Hours	Average Illuminance	Lux h	Mlux h	Average RH	Average Temp
TH & D	TH_1	0.25	6	50,163 ±517	300,981	0.30	17.2 ±1.4	42.5 ±1.7
TH & D	TH_2	0.50	12	50,417 ±1055	605,004	0.61	16.9 ±1.0	43.0 ±1.3
TH & D	TH_3	2	48	50,199 ±1216	2,409,552	2.41	19.0 ±2.4	41.2 ±2.3
TH & D	TH_4	4	96	50,261 ±1185	4,825,056	4.83	17.4 ±2.9	41.1 ±2.2
TH & D	TH_5	8	192	49,894 ±1271	9,578,648	9.58	17.9 ±2.4	42.4 ±2.4
TH & D	TH_6	16	384	49,788 ±1280	19,118,592	19.12	20.8 ±4.4	39.6 ±3.7
TH & D	TH_7	32	768	49,204 ±1414	37,788,672	37.79	19.5 ±3.8	41.3 ±3.2
TH & D	TH_8	64	1536	49,890 ±1473	76,631,040	76.63	22.5 ±4.5	37.9 ±4.5
TH & D	TH_9	128	3072	49,028 ±2747	150,614,016	150.61	22.6 ±4.4	35.3 ±4.9
LED1	LED1_1	0.25	6	48,900 ±61.3	293,398	0.29	26.0 ±0.6	33.9 ±0.7
LED1	LED1_2	0.50	12	48,845 ±71.3	586,143	0.59	25.6 ±0.6	34.5 ±0.8
LED1	LED1_3	2	48	48,912 ±112	2,347,776	2.35	27.0 ±1.9	34.1 ±0.9
LED1	LED1_4	4	96	48,523 ±403	4,658,208	4.66	25.1 ±2.7	33.6 ±0.9
LED1	LED1_5	8	192	48,155	9,391,104	9.39		
LED1	LED1_6	16	384	48,155	18,707,520	18.71		
LED1	LED1_7	32	768	47,603 ±755	36,559,104	36.56	30.9 ±5.0	32.6 ±2.4
LED1	LED1_8	64	1536	47,846 ±526	73,491,456	73.49	30.1 ±4.7	31.9 ±2.9
LED1	LED1_9	128	3072	47,895 ±424	147,133,440	147.13	28.1 ±5.4	30.6 ±3.2
LED2	LED2_1	0.25	6	48,426 ±89	290,556	0.29	25.5 ±0.9	34.4 ±0.9
LED2	LED2_2	0.50	12	48,364 ±89	580,365	0.58	25.0 ±0.8	35.1 ±0.9
LED2	LED2_3	2	48	48,456 ±163	2,325,888	2.33	26.4 ±1.8	34.5 ±1.0
LED2	LED2_4	3.9	94	48,579 ±353	4,566,426	4.57	24.8 ±2.4	34.0 ±1.0
LED2	LED2_5	7.8	187	49,612 ±1101	9,277,444	9.28	25.1 ±2.0	35.2 ±1.7
LED2	LED2_6	15.7	367	49,977 ±886	18,341,559	18.34	25.9 ±3.2	35.0 ±2.1
LED2	LED2_7	31.4	754	49,741 ±683	37,504,714	37.50	26.5 ±3.7	35.4 ±2.1
LED2	LED2_8	62.7	1505	50,397 ±1371	75,847,485	75.85	27.0 ±4.0	35.0 ±1.9
LED2	LED2_9	125.4	3010	51,090 ±1203	153,780,900	153.78	25.1 ±5.0	34.1 ±2.9
DL	DL_1	2	48	4,190	201,120	0.20	48.8 ±10.3	22.9 ± 5.0
DL	DL_2	4	96	6,177	592,992	0.59	43.5 ±11.0	24.1 ±7.0
DL	DL_3	8	192	5,636	1,082,112	1.08	45.6 ±10.4	24.2 ±6.2
DL	DL_4	16	384	5,866	2,252,544	2.25	46.6 ±11.0	24.5 ±7.1
DL	DL_5	32	768	5,135	3,943,680	3.94	48.0 ±10.9	24.7 ±6.3
DL	DL_6	64	1536	2,877	4,419,072	4.42	50.9 ±8.4	23.3 ±4.9
DL	DL_7	128	3072	1,757	5,397,504	5.40	47.8 ±10.0	22.6 ±4.7

Table 2 Average illuminance, temperature and relative humidity exposure at each sampling interval

All samples were dried in the dark for nine months at 20.1 ± 1.9 °C and 42.8 ± 7.1 % RH prior to initial analysis and subsequent exposure. Separate sets of samples were exposed to the three artificial light sources, giving an illuminance at the sample surface of 47-50,000 lux. This was taken to be reciprocal as it is well below the level at which Del Hoyo-Melendez (Del Hoyo-Melendez and others 2011) demonstrated the relationship to break down. Lux levels, temperature and relative humidity during the periods of exposure were monitored using Elsec 765C environmental loggers. Data was acquired every 10 minutes and the average values at each sampling interval for each chamber are included in Table 2. Diffusion tubes were used to monitor ozone and NO_x levels in each chamber throughout the period of exposure.

The two LED light boxes were cooled using both passive and active measures, namely heat sinks and fan system. The TH lamps were cooled using off the shelf heat sinks and fans. The halogen lamps were UV-filtered using a 4 mm polycarbonate sheet placed between the lamps and the samples. The control samples were masked from light exposure (Dark) with metal foil and placed within the TH light chamber, exposing them to the ambient temperature and RH conditions.

2.2 SAMPLE PREPARATION

2.2.1 Pigments

The lead chromate sulfate was supplied by BASF, cadmium sulfide was supplied by Kremer Pigments and the arsenic sulfide was an archival pigment from the Material Studies Laboratory, University College London. In all three cases their identity was confirmed using X-ray fluorescence and polarised light microscopy.

2.2.2 Watercolor Paints

Powder pigments were ground in deionised water to a thick, smooth paste, wetting with ethanol if necessary to avoid clumping. Gum Arabic was dissolved in water in a 1:2 w/w solution. The two were mixed together in a 1:1 v/v ratio, and then diluted with a varying amount of water to achieve a thin wash on paper. Paints were diluted so that a similar tone, or lightness, was achieved across all pigments. Paints were brushed out onto Arches 88 300 gsm paper in two strokes.

2.2.3 Oil Paints

Pigment powder was ground to a paste with sufficient Roberson cold pressed linseed oil according to its oil absorption index, values quoted in the Artists' Pigments series (Feller 1986; Fitzhugh 1997; Roy 1993). For painting out, if necessary, a paint vehicle (1 part turpentine to 2 parts linseed oil) was added drop-wise to achieve a similar consistency across all pigment mixtures. A manganese drier was added to poor drying paints at approximately 5% of the oil volume. The average pigment volume concentration (PVC) was around 0.36 (Table 3). Paint layers were drawn out onto a Teflon support with a flexible plastic edge and were of a thickness sufficient to give complete covering power.

Pigment	Weight in volume	PVC	Vol of drier	% of drier
Lead Chromate Sulfate	5 g in 1.8 mL	0.34	none	-
Arsenic Sulfide	2.5 g in 1.2 mL	0.38	0.06	5
Cadmium Sulfide	2.5 g in 1 mL	0.36	0.05	5

Table 3 Average pigment volume concentration

2.3 COLORIMETRY

Following nine months of drying in the dark initial colorimetry analysis was undertaken for each paint sample, with three replicate measurements on each sample taken before and after ageing. Markers were used to ensure that the sampling window could be repositioned on the same sampling location.

2.3.1 Color Difference

Reflectance spectra and colorimetric coordinate measurements were taken using a Konica Minolta CM-2600d color meter. The sample area was 3 mm in diameter, with an observer angle of 10°, a geometry that includes the specular reflectance component of the color measurement. The data were collected in L*a*b* Commission Internationale de l'Eclairage (CIE) coordinates using the standard illuminant D65. These coordinates referring to lightness (L*), red-green (a*) and yellow-blue (b*).

Color difference (ΔE_{00}) between a reference and a sample was calculated following the CIE ΔE 2000 method set out by Luo et al (Luo and others 2001).

Fixing a CIE ΔE (ΔE) value for ‘just noticeable change’ is problematic because the eye is variably sensitive to different parts of the color spectrum (Padfield 2014), which is difficult to account for in color metrics (de LEclairage 2004). Literature values for perceptible color shift (ΔE) range from 1 to 5 (Berger-Schunn 1994; Del Hoyo-Melendez and others 2011; Habekost 2013; Johnston-Feller 2001). With this in mind, here we set a boundary of $\Delta E_{00} = 2$ as a *clear discernible color shift*. For reference this boundary has been marked as a horizontal dashed line on all color shift plots.

Although the colorimeter allows for repositioning of the analysis location via a small viewing window, it has been previously shown (Luxford and Thickett 2012; Saunders and Kirby 2008) that limits of repeatability can be in the region of $\Delta E_{00} \approx 2$, which indicates that a measurement error in the region of human tolerance could be expected. Therefore consecutive color measurements on three sample spots were taken to determine the ΔE_{00} repeatability range for each control sample. The repeatability error for each paint is included in Table 4 and is an indication of the degrees of error in repositioning on the analysis window *and* sample homogeneity. For each pigment/binder combination only color shifts above the repeatability ΔE_{00} values presented can be ascribed to a real alteration in color. The same is true when establishing differences between the exposure type i.e. to say with certainty that a particular lamp has performed better or worse than another the lamps must exceed the specific ΔE_{00} repeatability value for a particular sample composition.

Pigment	Binder	Repeatability Error/ ΔE_{00}
Lead Chromate Sulfate	Gum Arabic	0.2 \pm 0.1
Arsenic Sulfide	Gum Arabic	0.2 \pm 0.2
Cadmium Sulfide	Gum Arabic	0.2 \pm 0.2
Lead Chromate Sulfate	Linseed Oil	0.8 \pm 0.1
Arsenic Sulfide	Linseed Oil	0.2 \pm 0.1
Cadmium Sulfide	Linseed Oil	0.5 \pm 0.4

Table 4 Measured error of repeatability of ΔE_{00} for the control samples

2.3.2 Change Index

Lunz et al. describe a damage index as ‘the fraction of the exposure that is required for a light source to induce the same level of color change’ (Lunz and others 2016). In their work values greater than one indicate a damage potential greater than the base source, although they describe their index as a ‘fraction’ of the exposure. Lunz et al. quote a single damage index value, assuming exponential behaviour across all samples.

Interpreting Lunz et al (Lunz and others 2016) work we report a similar *change index*¹ calculated at specific exposures; a single value for each curve was not possible given the varied fading behaviours across the sample sets. The change index (CI) gives the fraction of time required by each illuminant to reach an equivalent ΔE_{00} value, relative to the tungsten halogen source, *for each individual pigment*:

$$\Delta E_{00, \text{ref}} (\text{exposure} * CI_{\text{ref}}) = \Delta E_{00, \text{unknown}} (\text{exposure} * CI_{\text{unknown}})$$

Where $CI_{\text{ref}} = 1.00$ (1)

¹ The term ‘change’ rather than ‘damage’ was adopted to better encompass the potential for changes in colour due to continuing ‘drying’ of oil binders.

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3 Tungsten halogen exposure intervals of 2.4, 4.5 and 19.1 Mlux h were chosen as reference change
4 indices, avoiding extremely high exposure values that fall within regions of auto-retardation for some
5 samples. In contrast to Lunz et al. values greater than one indicate it takes *longer* for equivalent
6 change to be reached with the alternative source than for tungsten, i.e. such a light source may be less
7 damaging to that pigment. The score does not consider total irradiance, only illumination, and this
8 complexity should be acknowledged when comparing lighting systems (Cuttle 1996). It should also
9 be borne in mind that being a fraction, and therefore unit-less, it does not highlight whether the color
10 shift is perceptible. The change index tables provide only a guide and need to be cross-referenced with
11 the color shift curves.
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16 **2.4 FTIR-ATR**

17 To identify the chemical alterations associated with light-induced change, mid-infrared analysis was
18 carried out using a Bruker Alpha Fourier-transform infrared spectrometer (FTIR) fitted with a Bruker
19 Platinum diamond attenuated total reflectance (ATR) accessory, using Bruker OPUS software
20 version 7.5. A scan range of 400-4 000 cm^{-1} was employed, with a wavenumber resolution of 2 cm^{-1}
21 and scan accumulation of 32. Three replicates of each sample were acquired and averaged using
22 Thermo-Scientific GRAMS AI software version 9.1. FTIR analysis was carried out on all oil-based
23 samples by removing them from the Teflon substrate using a 3 mm Harris micro-punch and analysed
24 with the exposed paint surface in contact with the analysis crystal.
25
26

27 FTIR analysis was carried out on all oil-based samples. The gum Arabic paint samples were omitted
28 from FTIR analysis owing to the intense signal from the paper substrate masking the relatively weak
29 signal from the binder and pigments.
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33 **2.5 MULTIVARIATE ANALYSIS – PRINCIPAL COMPONENT ANALYSIS AND PARTIAL 34 LEAST SQUARES**

35 Principal component analysis (PCA) and partial least squares (PLS) were used to relate chemical
36 changes to exposure type, duration and color shift. Owing to the large dataset generated, this
37 multivariate approach was aimed at mapping spectral variations displayed across the infrared spectral
38 region and determining correlations across the sample set.
39
40

41 The initial principal component analysis data matrix (**X**) comprised of rows of FTIR spectral data
42 corresponding to the number samples in each data set, with each column of the matrix corresponding
43 to the number of variables, in this case wavenumber. In this work a 35 x 3 529 **X** matrix was
44 constructed for each pigment/oil binder composition relating to 35 samples (seven sampling intervals
45 for Dark, Daylight, TH, LED1 and LED2) and 3 529 wavenumbers. Individual matrices were
46 constructed for each pigment/oil binder composition to enable comparisons between the lighting
47 systems. This aimed to highlight inherent clustering related to exposure type and duration, and
48 establish the key variables impacting on such differences in principal component (PC) space.
49
50

51 Partial least squares is a regression method based on an iterative algorithm between two matrices, **X**
52 and **Y**. As before the **X** matrix relates to the spectral responses. Accompanying each **X** matrix were
53 two 35 x 1 **Y** matrices for PLS regression corresponding to the independent responses 1) level of
54 exposure (Mlux h) and 2) color shift (ΔE_{00}).
55

56 PCA and PLS was carried out using Camo Unscrambler X version 10.3. All FTIR spectra were pre-
57 processed to reduce variability caused by differences in scattering and background noise. All data
58 were smoothed using a Savitzky–Golay filter, fitting a 2nd order polynomial with an 11 point
59 symmetric window (Savitzky and Golay 1964). The smoothed spectra were then subsequently
60

1
2
3 normalized using Standard Normal Variate (SNV) (Fearn and others 2009; Muehlethaler and others
4 2011). Unless otherwise stated principal component analysis and partial least squares were carried out
5 on spectra spanning the entire mid-infrared region from 400-4 000 cm^{-1} , with a wavenumber
6 resolution of 2 cm^{-1} , equating to a total of 3 529 variables. Later iterations were performed on smaller,
7 truncated regions of the spectrum determined by the PCA loadings and PLS regression coefficient
8 plots of individual models. The data were mean centered and the models validated using the full
9 cross-validation method (Esbensen 2002).

10
11
12 Over optimistic calculations of principal components is as a common problem within multivariate
13 analysis (MVA) (De Maesschalck and others 1999). Therefore each model was calculated with a total
14 of seven components, however, later principal components were often dominated by interference and
15 therefore not reported on.

16 17 18 19 **3. RESULTS AND DISCUSSION**

20 21 **3.1 LEAD CHROMATE SULFATE ($\text{PbCrO}_4 \cdot x\text{PbSO}_4$) IN GUM ARABIC**

22 Color shift across all sample exposures appear to be equivalent and follow similar patterns of change;
23 the tungsten halogen (TH) lamps performing somewhat better at exposures exceeding 4.5 Mlux h
24 (Fig. 2). On Initial exposure there is a relatively rapid change in ΔE_{00} , reaching levels of $\Delta E_{00} \approx 3.5$ at
25 exposures of 9.5 Mlux h. After this point there is an apparent plateau in ΔE_{00} across all samples until
26 the final sampling interval of 150 Mlux h, where LED1 display a slight increase in ΔE_{00} . Across all
27 sampling intervals the TH samples display higher standard deviations compared to the other sample
28 sets. When considering the reproducibility error is low for lead chromate sulfate in gum Arabic this
29 indicates sample inhomogeneity.

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31
32 Fig. 2 Color shift (ΔE_{00}) for lead chromate sulfate in gum Arabic exposed to TH, LED1 and LED2.
33 Horizontal dashed line denotes a clear discernible color shift

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37 The changes in color are due to a decrease in the L^* and b^* coordinates, both of which follow a
38 similar pattern of behaviour as ΔE_{00} ; in initial decrease in L^* and b^* , followed by a plateau. The
39 samples display a rapid darkening, which is independent of exposure type, and a shift to a more blue
40 hue ($-b^*$) (Fig. 3).

41
42 Fig. 3 Color shift (Δa^* and Δb^*) for lead chromate sulfate in gum Arabic exposed to TH, LED1 and
43 LED2

44
45
46 Up to 0.5 Mlux h the samples exposed to daylight exhibit a marginally higher color shift compared to
47 those exposed to TH, LED1 and LED2, although ΔE_{00} is borderline with levels of discernible change.
48 Between 1-4.8 Mlux h all four light exposures are equivalent (Table 5).

49 50 51 52 **3.2 LEAD CHROMATE SULFATE ($\text{PbCrO}_4 \cdot x\text{PbSO}_4$) IN LINSEED OIL**

53 On exposure to tungsten halogen the samples display a perceptual increase in ΔE_{00} up to exposure
54 levels of 37.5 Mlux h (Fig. 4). After this exposure, the color shift plateaus and remains constant
55 (within error) up to 150 Mlux h. This color shift is due to a significant decrease in the L^* , a^* and b^*
56 coordinates, namely a darkening of the paint coupled with a shift in hue to a more green and blue
57 paint layer (Fig. 5 and Supplementary Information 2). This behaviour is mirrored by the samples
58 exposed to both LED lamps; color shift is equivalent across all samples when accounting for
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3 repeatability error, standard deviation and levels of discernible change. At 150 Mlux h there is a slight
4 increase and divergence in ΔE_{00} values for the LED1 samples, which is mirrored in the L^* , a^* and b^*
5 coordinates.
6

7 Fig.4 Color shift (ΔE_{00}) for lead chromate sulfate in linseed oil exposed to TH, LED1 and LED2.
8 Horizontal dashed line denotes a clear discernible color shift.
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10
11 Fig. 5 Color shift (Δa^* and Δb^*) for lead chromate sulfate in linseed oil exposed to TH, LED1 and
12 LED2
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15 The alterations in color displayed at low to moderate exposures are not significantly different between
16 the three artificial ageing regimes. At 150 Mlux h there is a divergence in the values of ΔE_{00} , with
17 LED1 displaying marginally poorer performance and discernible difference to the LED2 and TH
18 samples. It is worth noting that at exposures above 9.5 Mlux h the color shift in the gum Arabic
19 samples is approximately two thirds lower than the equivalent linseed oil samples. Although it might
20 be reasonable to expect greater change in watercolor layers due to the double exposure through
21 reflection of the paper, the large contribution from the underlying paper in the translucent watercolor
22 will have a significant impact on ΔE_{00} compared to the opaque linseed oil paint. The dominance of the
23 paper through the thin watercolor layers might also cause a less perceptible change.
24

25 The samples exposed to filtered daylight exhibit a significant increase in ΔE_{00} compared to the TH,
26 LED1 and LED2 samples. The deviations are higher, but still significant after daylight exposure, with
27 ΔE_{00} values averaging 6.2 at 2.3 Mlux h, compared to $\Delta E_{00} \approx 2.4$ for the other three exposures. At low
28 exposure levels the daylight samples exhibit a marked increase in ΔE_{00} relative to the artificially aged
29 samples (Table 5).
30

31 The FTIR analysis shows the appearance of a spectral band centred at 470 cm^{-1} with increasing
32 exposure, which is attributed to the formation of PbO_2 (Gautam and others 2012) (Fig. 6). The exact
33 route of this photochemical reaction is still not fully understood, but it has been proposed that lead
34 chromate is reduced to chrome oxide and lead oxide (Erkens and others 2001; Monico and others
35 2011). Whatever the precise mechanism, it is clear from the spectra that the Pb-O band at 470 cm^{-1}
36 increases with exposure time across all artificial exposures, namely TH, LED1 and LED2.
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39 Fig. 6 Lead chromate sulfate expanded spectra for Control (black) and TH, LED1 and LED2 samples
40 at exposure intervals 4 and 9
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43 The distinct relationship between exposure and the increase across this particular spectral region was
44 further interrogated using partial least squares to determine whether the measured levels of exposure
45 (Mlux h) could be quantitatively correlated with the FTIR spectra and the formation of PbO_2 . A PLS
46 model was calculated regressing the variable region from $400\text{-}650 \text{ cm}^{-1}$ against Mlux h for the
47 Control, TH, LED1 and LED2 samples.
48

49 The corresponding regression coefficients for the first and third axes were shown to be influenced by
50 470 cm^{-1} , in addition to an inverse relationship between variables 595 cm^{-1} and 610 cm^{-1} in the case of
51 the third axis (Supplementary Information 3). The bands at 595 cm^{-1} and 610 cm^{-1} are attributed to
52 SO_4^{2-} bending modes (Lane 2007) and the intensity of these were also shown by Monico et al
53 (Monico and others 2011) to invert during the ageing of lead chromate sulfate.
54

55 The FTIR analysis and partial least squares regression demonstrates the increasing presence of
56 degradation products in the lead chromate sulfate, namely lead oxide (Fig. 7). Direct correlations were
57 found between the spectral ageing patterns, specifically the spectral band centered at 470 cm^{-1} , and the
58 duration of exposure and color shift. This correlation ($R^2 = 0.94$) was particularly evident in the
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3 samples exposed to LED1 and is in keeping with the marginally higher ΔE_{00} values shown at high
4 exposures to LED1 (Fig. 4).
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6 Fig. 7 Lead chromate sulfate PLS predicted versus measured validation line for Mlux h with three
7 Factors for LED1. Regression line (grey) $R^2 = 0.94$ and target line (black) $R^2 = 1.00$
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10 3.3 ARSENIC SULFIDE (As_2S_3) IN GUM ARABIC

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12 The repeatability error is low compared to the degree of color shift in the arsenic sulfide samples kept
13 in the dark, suggesting that the fluctuations in ΔE_{00} are not due to sampling errors (Table 4 and Fig. 8).
14 However, the standard deviation is large. It should be borne in mind that orpiment is a ground mineral
15 pigment, and the particle size range is broad, giving a heterogeneous surface topography. Differences
16 in color shift are likely to be influenced by alterations in scattering as a result of drying, which is
17 *physical* change. On initial exposure the Dark samples show an apparent increase in ΔE_{00} followed by
18 a temporary decrease. This initial increase is concomitant with a decrease in the a^* coordinate,
19 suggesting the formation of a greener paint layer on drying (Fig. 9).
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22 Fig. 8 Color shift (ΔE_{00}) for arsenic sulfide in gum Arabic exposed to TH, LED1 and LED2.
23 Horizontal dashed line denotes a clear discernible color shift
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25 Fig. 9 Color shift (Δa^* and Δb^*) for arsenic sulfide in gum Arabic exposed to TH, LED1 and LED2
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28 The standard deviations at each sampling interval are high, making interpretation tentative. However,
29 all samples exhibit a decrease in a^* , indicating the formation of a greener pigment layer as exhibited
30 in the Control samples. Up to exposures approximating 4.5 Mlux h all three artificial lighting systems
31 are equivalent and below the limits of visual detection (Fig. 8). Between 9.5 Mlux h and 73 Mlux h
32 LED1 appears to perform marginally better than the TH and LED2. All three light exposures exhibit a
33 significant decrease in the b^* coordinate, equating to a loss of yellow and a shift towards a blue hue
34 (Fig. 9). At very high exposures, above 75 Mlux h this increase in blueness is retarded on exposure to
35 the TH lamps. This is supported by the ΔE_{00} values and indicating that at high exposures arsenic
36 sulphide in gum Arabic is more stable under TH lighting.
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39 When accounting for the high standard deviations, the samples exposed to filtered daylight display
40 equivalent levels of color shift.
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43 3.4 ARSENIC SULFIDE (As_2S_3) IN LINSEED OIL

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45 The standard deviations and repeatability errors are low, indicating a homogenous surface and color
46 shift across all samples. At exposures up to 9.5 Mlux h all three artificial lighting exposures show
47 similar levels of change, $\Delta E_{00} \approx 1.0$ (Fig. 10). At higher exposures there is a divergence, with the TH
48 and LED2 samples exhibiting a greater color shift than the LED1 samples.
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51 Fig. 10 Color shift (ΔE_{00}) for arsenic sulfide in linseed oil exposed to TH, LED1 and LED2.
52 Horizontal dashed line denotes a clear discernible color shift
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55 The LED2 samples demonstrate a clear, perceptual color shift above 18.5 Mlux h. The change in color
56 is due to a decrease in L^* and b^* , and an increase in a^* . This latter change in hue is in opposition to
57 the decrease in a^* exhibited by the TH and LED1 samples (Fig. 11). The former lamp induces redder
58 color shift, whilst the TH and LED1 lamps tend towards a greener shift in hue.
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Fig. 11 Color shift (Δa^* and Δb^*) for arsenic sulfide (orpiment) in gum Arabic exposed to TH, LED1 and LED2

The discoloration of arsenic sulphide (orpiment) is well documented and known to form the more stable arsenic oxide compound, arsenolite (As_2O_3), particularly on exposure to wavelengths shorter than 428 nm (Allen and others 2005). Whitmore and Cass (Whitmore and Cass 1989) have also suggested there may be a link between the presence of nitrogen dioxide and accelerated deterioration of both orpiment (As_2S_3) and realgar (As_4S_4). The concentrations of nitrogen dioxide were equivalent inside all three light chambers. Therefore, the measured color shift is likely due to the higher spectral power distribution between the 380-429 nm in the LED2 lamps

Fig. 12 shows the appearance an FTIR band at 790 cm^{-1} that confirms the formation of arsenic oxide (As_2O_3) (Paiuk and others 2012; Vermeulen and others 2016), accompanied by a band an As-O vibration at 1030 cm^{-1} . There were no bands associated with arsenic sulfide due to its absorbance frequencies being outside of the mid-infrared region.

Fig. 12 Expanded arsenic sulfide spectra for Control (black) and TH samples at exposure interval 4 (grey solid) and 9 (grey dashed)

To interrogate the alterations in the infrared spectra following exposure the color shift data was regressed against the primary FTIR variables using PLS. Fig. 13 shows the predicted versus measured validation line for ΔE_{00} , indicating a high degree of correlation between the FTIR and colorimetry analysis ($R^2 = 0.97$). The associated regression coefficient plots for principal axes one to four are dominated by the band centred at 790 cm^{-1} , associated with the formation of arsenic oxide (As_2O_3). This is a clear indication that the color shift of the arsenic sulfide oil paint is primarily driven by the degradation of the orpiment pigment (Vermeulen and others 2016) and exacerbated by exposure to LED2.

Fig. 13 Arsenic sulfide PLS predicted versus measured validation line for ΔE_{00} with four Factors. Regression line (black) $R^2 = 0.97$ and target line (black) $R^2 = 1.00$

3.5 CADMIUM SULFIDE (CdS) IN GUM ARABIC

Accounting for repeatability error and levels of perceptual change, the samples kept in the dark exhibited no significant color shift (Fig. 14). The same is true for the TH, LED1 and LED2 samples. Although there were slight increases in ΔE_{00} the maximum value across all three samples sets was $\Delta E_{00} = 0.9$, which is below the limit of discernible change. The samples exposed to UV filtered daylight followed the equivalent behaviour to the other exposed sample sets.

Fig. 14 Color shift (ΔE_{00}) for cadmium yellow in gum Arabic exposed to TH, LED1 and LED2. Horizontal dashed line denotes a clear discernible color shift.

3.6 CADMIUM SULFIDE (CdS) IN LINSEED OIL

The TH, LED1 and LED2 samples displayed slight increases in ΔE_{00} when compared to the control samples, with the maximum value across all three samples sets reaching $\Delta E_{00} = 1.4$ (Fig. 15). Although this is potentially a detectable change in color, when considering the error of repeatability and the similarities across all of the exposed samples these differences are not significant. The minor changes detected are due to a positive shift in the L^* and b^* axes, and a negative change in the a^*

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3 coordinate, equating to a lightening of the paint surface and a slightly more green/yellow hue (Fig.
4 16).

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6 Fig. 15 Color shift (ΔE_{00}) for cadmium yellow in linseed oil exposed to TH, LED1 and LED2.
7 Horizontal dashed line denotes a clear discernible color shift

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9 Fig. 16 Color shift (Δa^* and Δb^*) for cadmium yellow in linseed oil exposed to TH, LED1 and LED2

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12 Leone and Burnstock (Leone and others 2005) and Mass et al (Mass and others 2013) demonstrated
13 that CdS was susceptible of chemical alterations in the pigment structure on exposure to light and
14 high RH (85%), which resulted in the formation of brown, white and colorless compounds. Eastaugh
15 (Eastaugh 2008) also suggests moisture may have a deleterious effect on the pigment if only leanly
16 bound in the paint. However, Leone and Burnstock found that alterations were dependant on the
17 physical conformation of the pigment and where there was a higher content of amorphous cadmium
18 sulfide the pigment was more prone to deterioration. Although there were some changes to the color
19 of the CdS samples, these were very low considering the degree of exposure of the samples. The
20 reason for apparent stability across all lighting types is potentially twofold, namely the low relative
21 humidity within each ageing chamber and quality of the manufactured pigment, which is likely to
22 have a high degree of crystallinity. The samples exposed to filtered daylight followed the equivalent
23 behaviour.

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27 The initial principal component analysis across the entire spectral range displayed no inherent clusters
28 or patterns relating to exposure type or duration, although there was evidence of the exposed samples
29 clustering away from the control samples kept in the dark (data not shown). Following variable
30 selection the overall description of the samples improved, with the explained variance at two
31 components increasing from 87 % to 93 %. Primary variables influencing clustering were 1740 cm^{-1} ,
32 2850 cm^{-1} and 2922 cm^{-1} ; the first exhibiting an inverse relationship to the latter variables. The band at
33 1740 cm^{-1} is assigned to the C=O stretch associated with ester linkages formed during oxidative
34 polymerisation of fatty acid materials i.e. linseed oil, whilst the bands at 2850 cm^{-1} and 2922 cm^{-1}
35 suggest the loss of hydrocarbon. A reduction in the intensity of the CH₂ bands 2850 cm^{-1} and 2922 cm^{-1}
36 is in line with oxidative chain cleavage (Meilunas and others 1990). There was no systematic
37 clustering associated with exposure to particular light sources and no evidence of alterations in the
38 chemical structure of cadmium sulfide (Mass and others 2013) or the presence of pigment and oil
39 binder interactions (Pouyet and others 2015). All molecular changes on exposure were ascribed to the
40 oxidation and polymerisation reactions associated with the continued drying of linseed oil.
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Pigment	Binder	TH Reference Exposure/Mlux h	CI TH	CI LED1	CI LED2	CI DL
Lead Chromate Sulfate	Gum Arabic	2.4	1.00	1.10	0.70	0.77
Lead Chromate Sulfate	Gum Arabic	4.8	1.00	0.98	1.09	0.97
Lead Chromate Sulfate	Gum Arabic	19.1	1.00	0.73	0.77	N/A
Arsenic Sulfide	Gum Arabic	2.4	1.00	0.72	2.07	0.58
Arsenic Sulfide	Gum Arabic	4.8	1.00	1.59	1.70	0.62
Arsenic Sulfide	Gum Arabic	19.1	1.00	3.37	1.15	N/A
Cadmium Sulfide	Gum Arabic	2.4	1.00	7.05	5.94	3.94
Cadmium Sulfide	Gum Arabic	4.8	1.00	1.35	2.61	1.52
Cadmium Sulfide	Gum Arabic	19.1	1.00	0.49	0.42	N/A
Lead Chromate Sulfate	Linseed Oil	2.4	1.00	0.78	0.93	0.30
Lead Chromate Sulfate	Linseed Oil	4.8	1.00	0.99	0.83	0.40
Lead Chromate Sulfate	Linseed Oil	19.1	1.00	0.90	0.75	N/A
Arsenic Sulfide	Linseed Oil	2.4	1.00	0.90	0.84	0.33
Arsenic Sulfide	Linseed Oil	4.8	1.00	2.06	1.59	0.42
Arsenic Sulfide	Linseed Oil	19.1	1.00	1.59	0.84	N/A
Cadmium Sulfide	Linseed Oil	2.4	1.00	0.77	0.70	0.81
Cadmium Sulfide	Linseed Oil	4.8	1.00	0.61	0.78	3.41
Cadmium Sulfide	Linseed Oil	19.1	1.00	0.78	1.11	N/A

Table 5 Change Index: fraction of exposure required to induce an equivalent color change to the TH reference at a given exposure (Mlux h)

4. CONCLUSIONS

The use of LED lighting in heritage institutions is steadily increasing due to their energy efficiency, long lamp life and the risk of obsolescence of tungsten halogen lighting. Therefore, understanding the stability of pigments and paints exposed to specific spectral distributions is critical for safeguarding works of art. The results presented here on three historically important yellow pigments suggest that both lead chromate sulphate and arsenic sulphide in linseed oil display an increased risk to the formation of oxidative degradation products on exposure to LED lighting.

The FTIR analysis and partial least squares regression demonstrated the presence of degradation products in lead chromate sulfate, namely lead oxide. A correlation between exposure and oxidation was particularly evident in the samples exposed to LED1 and was in keeping with the marginally higher ΔE_{00} values at very high exposures. Lead chromate sulfate in gum Arabic displayed discernable color shift above 2 Mlux h, with the TH samples displaying marginally lower degrees of change, although when accounting for deviations this may not be significant.

Color shifts of arsenic sulphide in linseed oil indicated that, at high exposures, the LED2 lamps induced a definite shift in color compared to samples exposed to TH and LED1. This was due to the

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3 transformation of arsenic sulfide into arsenic oxide, accelerated by the higher spectral distribution
4 across the 380-429 nm region. This interpretation was supported by the FTIR analysis that clearly
5 demonstrated the presence of arsenic oxide at higher exposures and indicated a correlation between
6 the exposure type, duration and color shift. The colorimetry data for arsenic sulphide in gum Arabic
7 were inconclusive due to the high deviations across all samples sets caused by large particle size and
8 surface heterogeneity.

9
10 The cadmium sulfide samples bound in linseed and gum Arabic displayed very low level,
11 insignificant alterations in color across all sample sets. This was attributed to the high quality of the
12 manufactured pigment and the low relative humidity in each ageing chamber. Further work is
13 underway to investigate the stability of low quality, high amorphous content cadmium sulphide on
14 exposure to LED lighting.

15
16 This work forms a proportion of larger research project aimed at interrogating the impact of LED
17 lighting on model pigment and paint compositions and the results from the broader project will be
18 published in due course. Although the work presented here has been limited to three pigments and two
19 binders, the initial results indicate that certain colorants are more vulnerable to degradation when
20 exposed to LED lighting. As such, strategies for the display of works of art will need to carefully
21 balance curatorial needs with those of particular pigment types. Decisions regarding the length of time
22 an object is on display will continue to be critical, but will also need to take into account the type of
23 LED used for display.

24 25 26 27 **5. FUNDING**

28
29 E Richardson was funded by the Heritage Protection Commission (Grant Number 7087) and the
30 Analytical Chemistry Trust Fund (Grant Number TWAf/15/01): "Assessing the Impact of LED
31 Lighting on Pigments and Paper in Collections."
32

33 34 35 **6. DISCLOSURE STATEMENT**

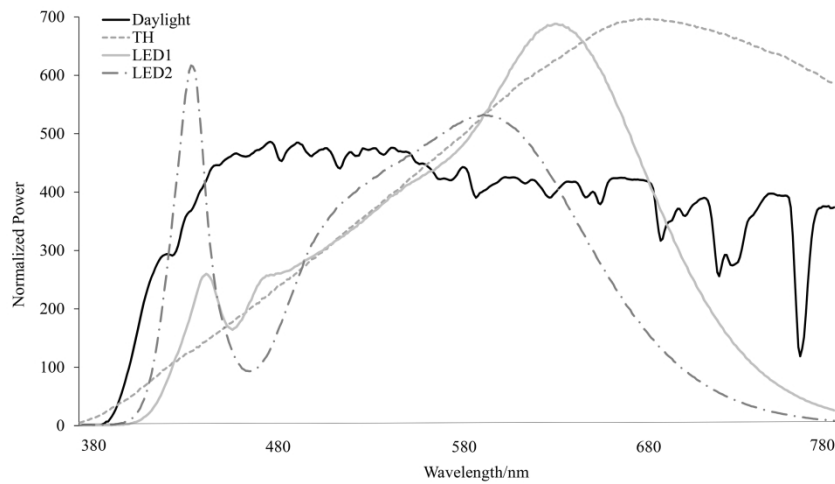
36
37 The authors have no financial interests to declare
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40 41 **7. REFERENCES**

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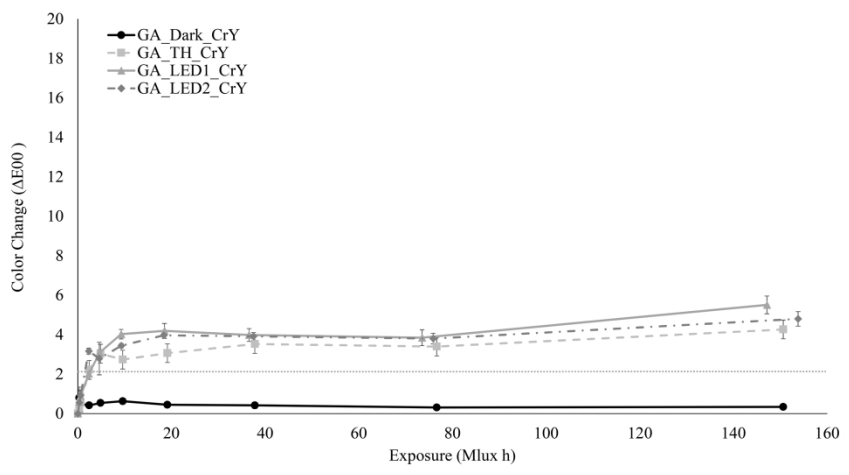
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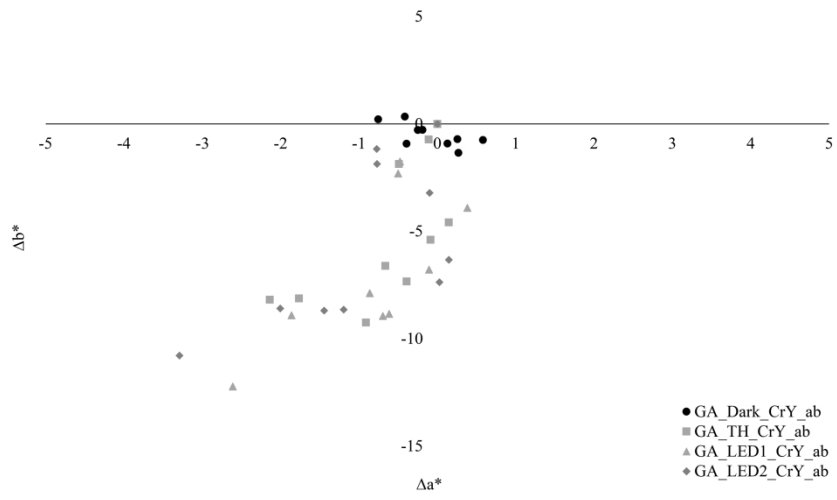
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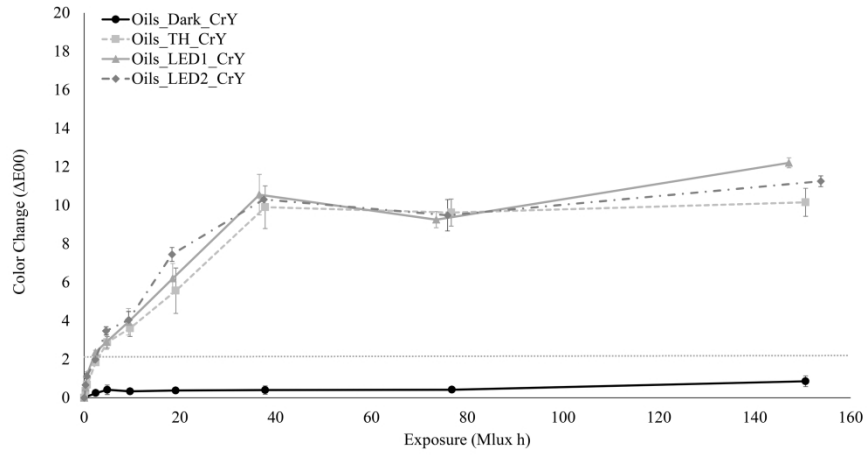
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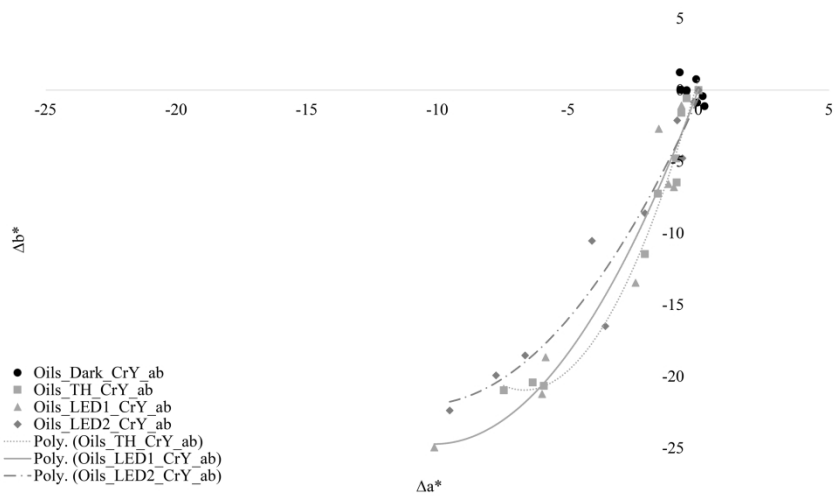


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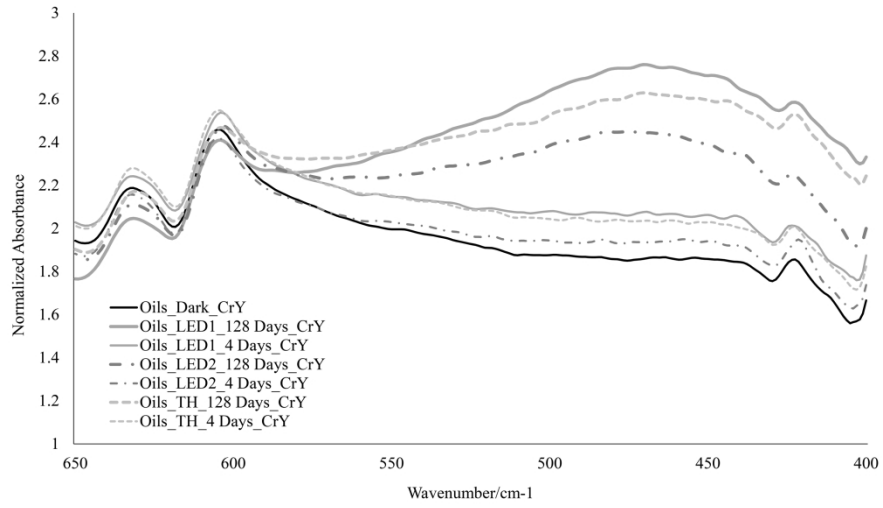


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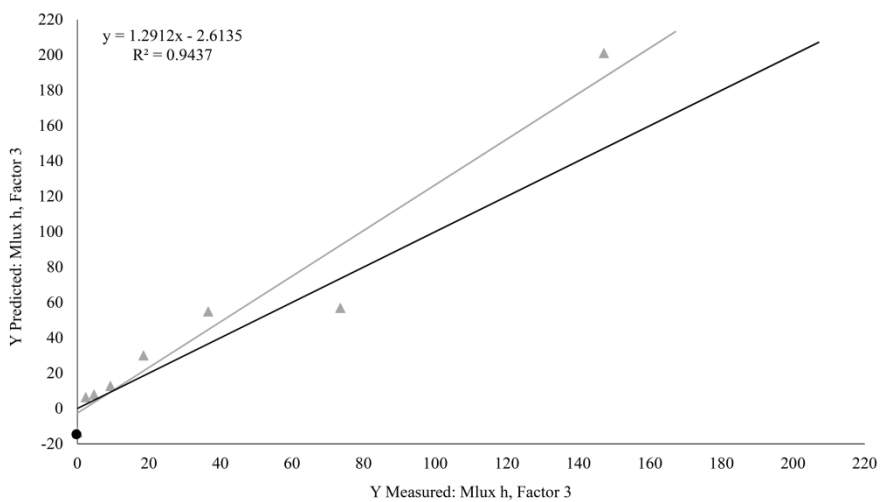


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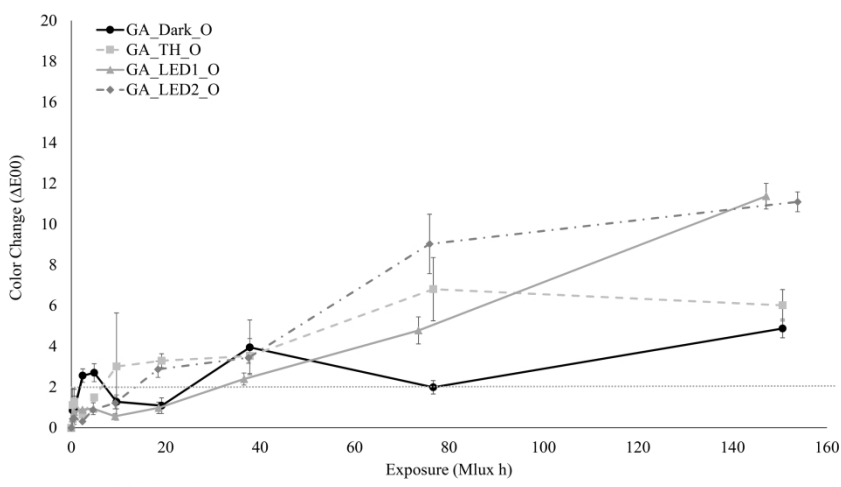


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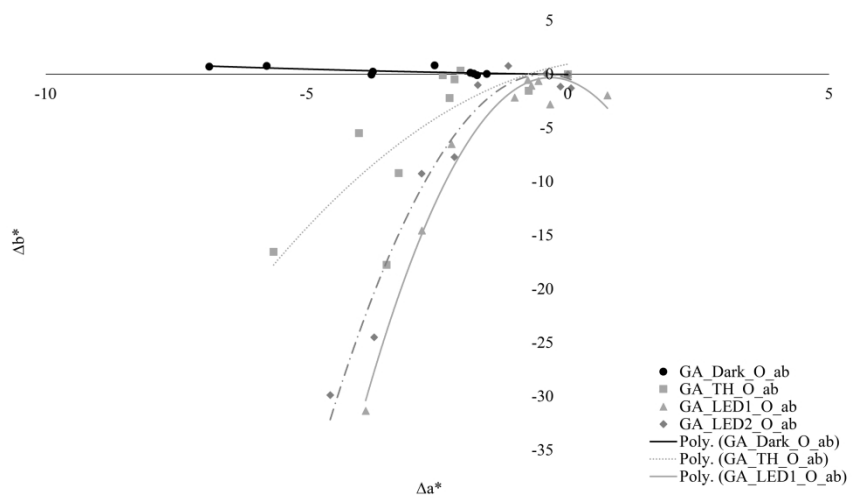


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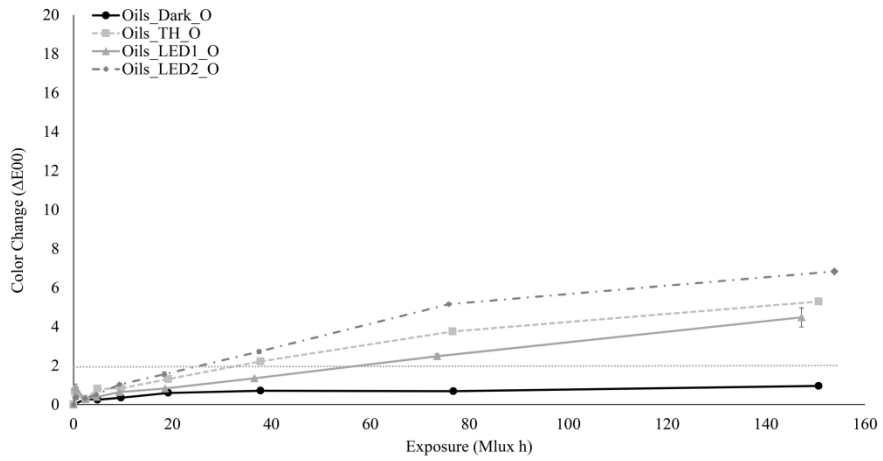


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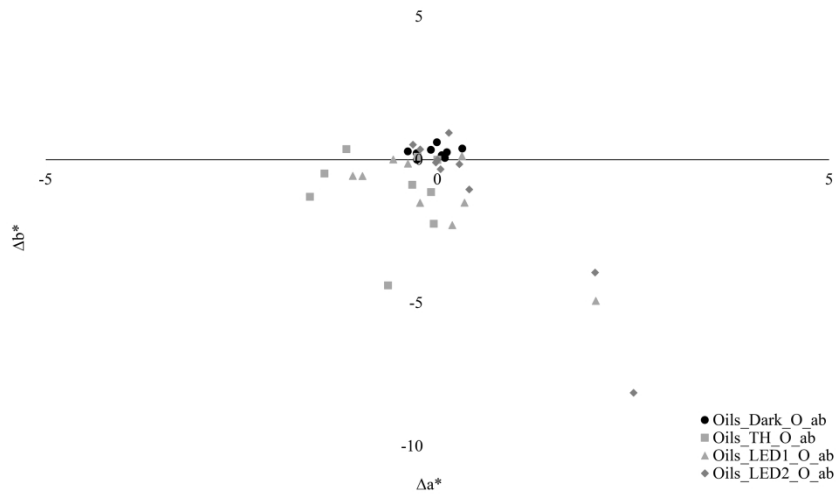
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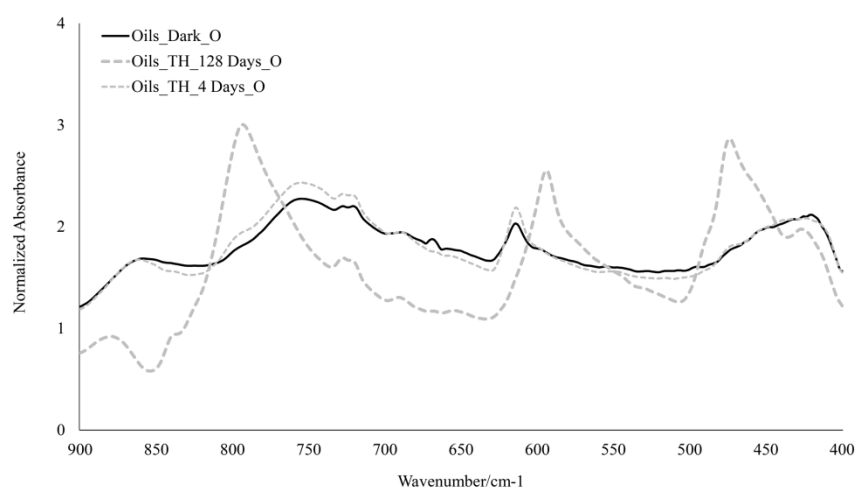
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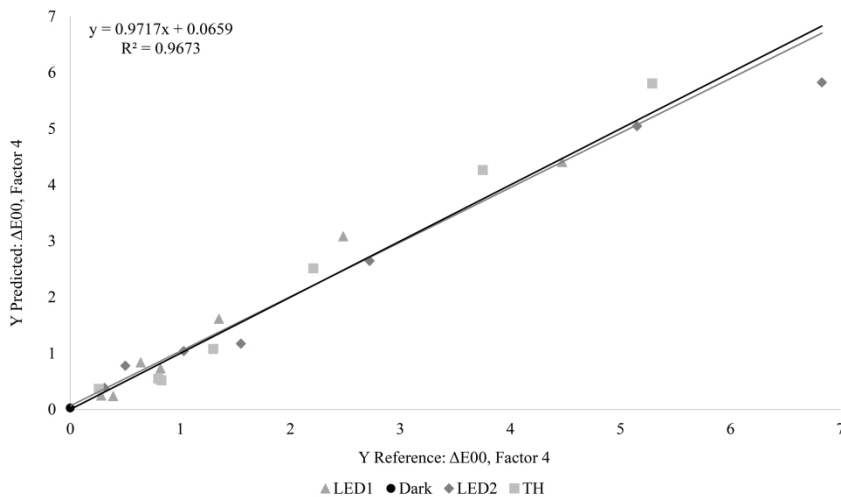


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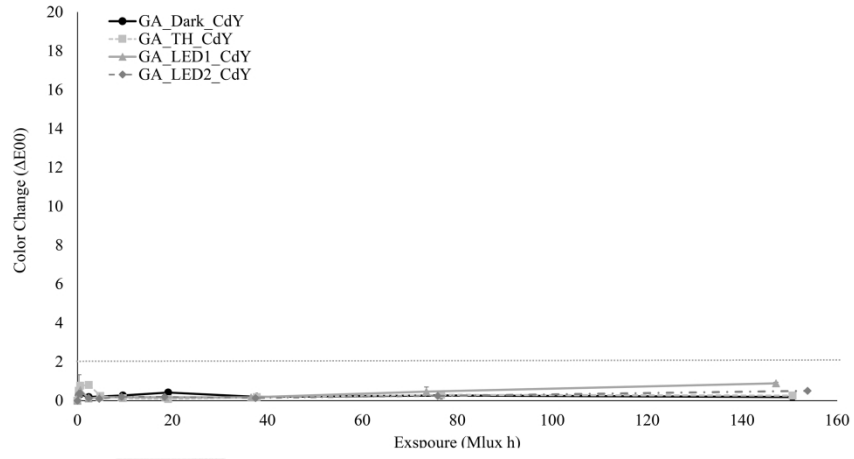


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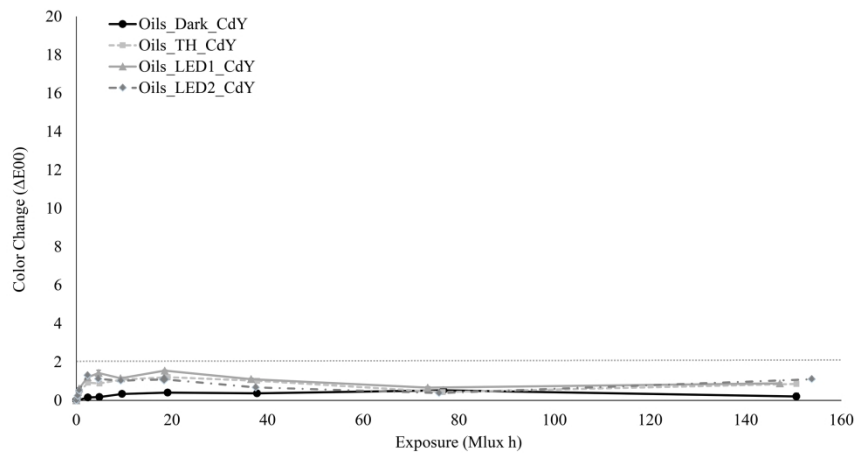


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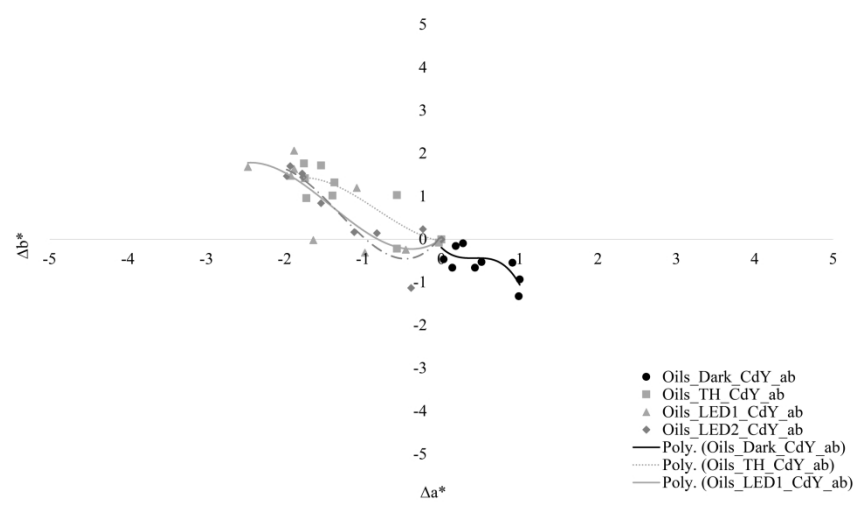


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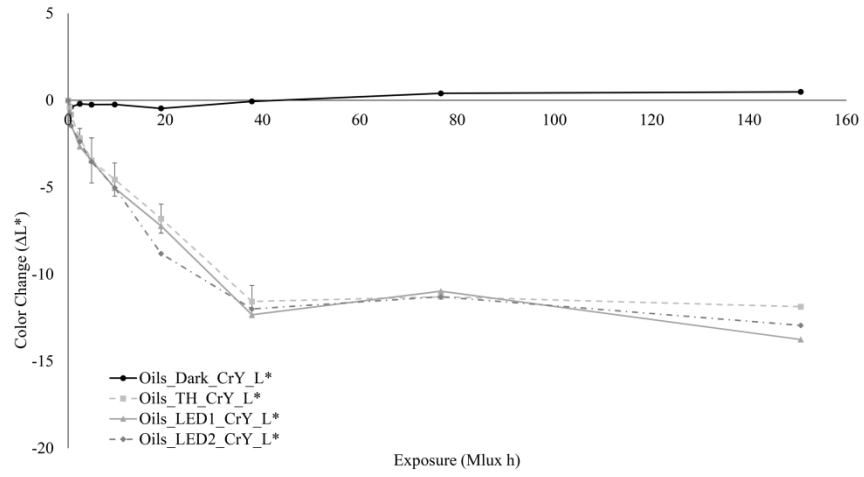
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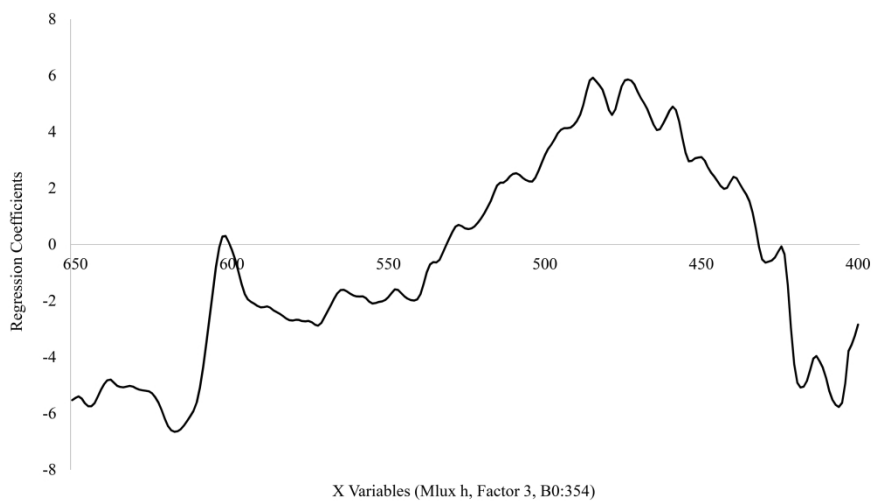
Prussian blue & lead carbonate
 Prussian blue
 Indigo & lead carbonate
 Indigo
 Cadmium sulfide
 Arsenic sulfide (orpiment)
 Lead chromate sulfate
 Red lead
 Vermilion
 Carmine Lake
 Madder Lake
 Lead carbonate
 Linseed oil

SI. 1 Example of linseed oil paint swatches prior to light exposure

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SI. 2 Color shift (ΔL^*) for lead chromate sulfate in linseed oil exposed to TH, LED1 and LED2
297x167mm (300 x 300 DPI)



SI 3: Lead chromate sulfate PLS Model 1 Regression Coefficient plot for factor three

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