



International Commission on Illumination  
Commission Internationale de l'Eclairage  
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**PO048**

**EXPERIMENTAL STUDY ON CHEMICAL AND  
COLORIMETRIC CHANGES OF ART MATERIALS BY LED  
IRRADIATION**

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DOI 10.25039/x46.2019.PO048

from

CIE x046:2019

Proceedings  
of the

29th CIE SESSION

Washington D.C., USA, June 14 – 22, 2019

(DOI 10.25039/x46.2019)

The paper has been presented at the 29th CIE Session, Washington D.C., USA, June 14-22, 2019. It has not been peer-reviewed by CIE.

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## EXPERIMENTAL STUDY ON CHEMICAL AND COLORIMETRIC CHANGES OF ART MATERIALS BY LED IRRADIATION

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DOI 10.25039/x46.2019.PO048

### Abstract

The main focus of the research presented in this paper was the investigation of the effect of LED-lighting on some art paint colours by reproducing indoor museum conditions applied on art materials. A series of inorganic pigments and organic binders were selected and mixed in different ratio for obtaining 2-components paint mock-ups thus as much as possible allowing to reproduce the paint colours used in modern and contemporary art. Three different systems were employed for light exposure of the prepared samples with different content between 410 nm and 490 nm. To analyse colour changes of the pigments, spectrophotometry was adopted. Chemical stability of the materials was investigated using Pyrolysis - Gas Chromatography / Mass Spectrometry (Py-GC/MS), also in Thermally assisted Hydrolysis and Methylation mode (THM-GC/MS), and Fourier Transform Infrared Spectroscopy in Attenuated Total Reflection (FTIR-ATR) mode. Additionally,  $\mu$ -Raman spectroscopy was used.

*Keywords:* modern paint ageing, museum lighting, Py-GC/MS, spectrophotometry, FTIR-ATR,  $\mu$ -Raman spectroscopy

### 1 Introduction

Indoor museums exhibiting paintings need proper illumination systems to provide the best possible viewing conditions and a comfortable atmosphere for visitors, while avoiding the harmful effects of optical radiation on the paintings. CIE published guidelines (CIE, 1990) (CIE, 2004) for illumination of different artworks in which art conservation aspects are also discussed besides visual aspects. According to these guidelines the colour changes of light sensitive materials depend on irradiation, spectral power distribution, spectral responsivity of the given material and duration of exposure. The CIE Report 157:2004 covers both the heating effects and photochemical effects on the materials, and enumerates the relative damage potential of different light sources by giving a formula on the calculation of the damage potential. These guidelines did not consider LED lighting as an alternative for museum lighting, thus being applicable mainly for the traditional light sources.

In this paper, a series of experiments are presented for the investigation of damaging effects of LED lighting on paint materials. In order to determine any changes on the surface of the paint material as well as in the paint structure caused by the exposure to the different illumination systems, reflectance measurements,  $\mu$ -Raman, FTIR-ATR, and Py-GC/MS analytical techniques were used.

The investigation was carried out within the Bilateral Research Project - between the Light and Colour Science Research Laboratory of the University of Pannonia, Veszprém, Hungary and the Institute of Science and Technology in Art at the Academy of Fine Arts, Vienna, Austria.

### 2 Experimental setup

#### 2.1 Selection of pigments and binding media for the paints

"2-components self-made paint" mock-ups were prepared by mixing inorganic pigments (P) powders (Kremer Pigmente, Germany) with an alkyd (Medium 4 - Lukas, Germany), acrylic

(Plextol D498 - Kremer Pigmente, Germany) and linseed oil (Kremer Pigmente, Germany) binding media in different ratio depending on the consistence of the paint achieved. The paints were applied on microscope glass slides (30 mm x 20 mm) in a painted area of 30 mm x 20 mm, obtaining a thickness of 150  $\mu\text{m}$ , and left drying at room conditions for eight weeks. The same procedure was used to prepare mock-ups of pure binding media, without addition of pigments. Figure 1 shows the prepared samples.

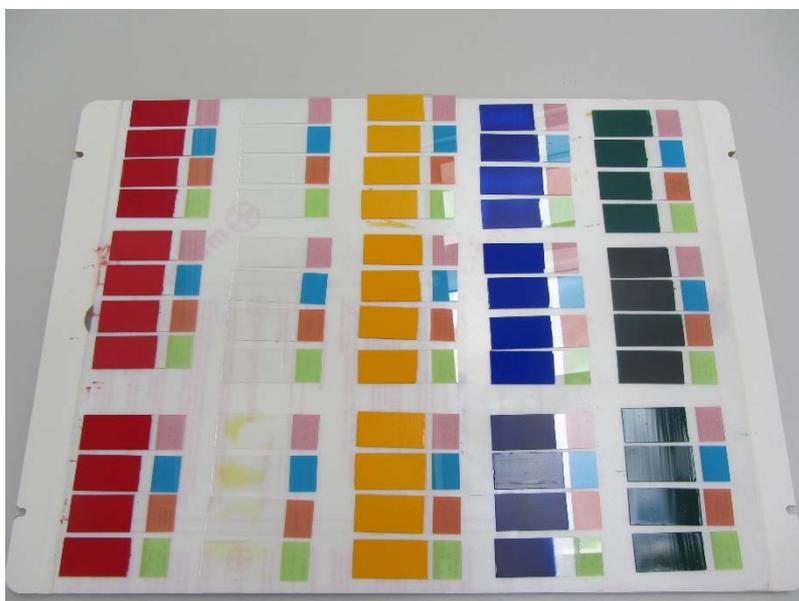


Figure 1 – Overview of the prepared samples

## 2.2 Light exposure conditions

In the experiments two lighting both with 20-channel spectrally tuneable LED luminaires were used. The luminaires have 17 monochromatic LED channels and 3 types of white phosphor LEDs. Peak wavelengths of the channels are in the 414 nm – 691 nm range. Figure 2 illustrates the SPDs of each LED channel of the luminaire. Each channel contains 24 LEDs giving a total of 480 LEDs per luminaire. The third lighting booth contained a set of cold mirror incandescent halogen lamps, which is a widely used light source in museum environment.

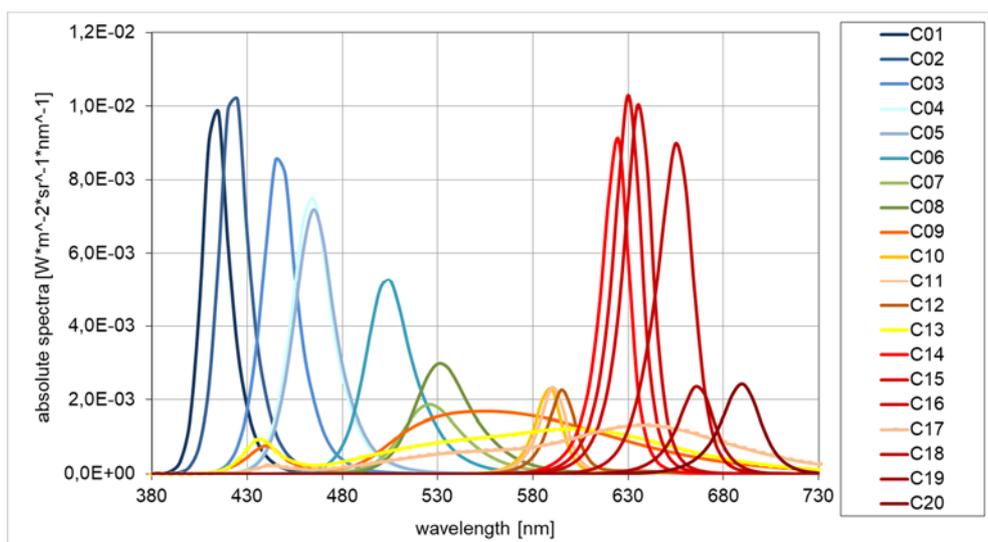


Figure 2 – LED channel SPDs of the tuneable lighting booths

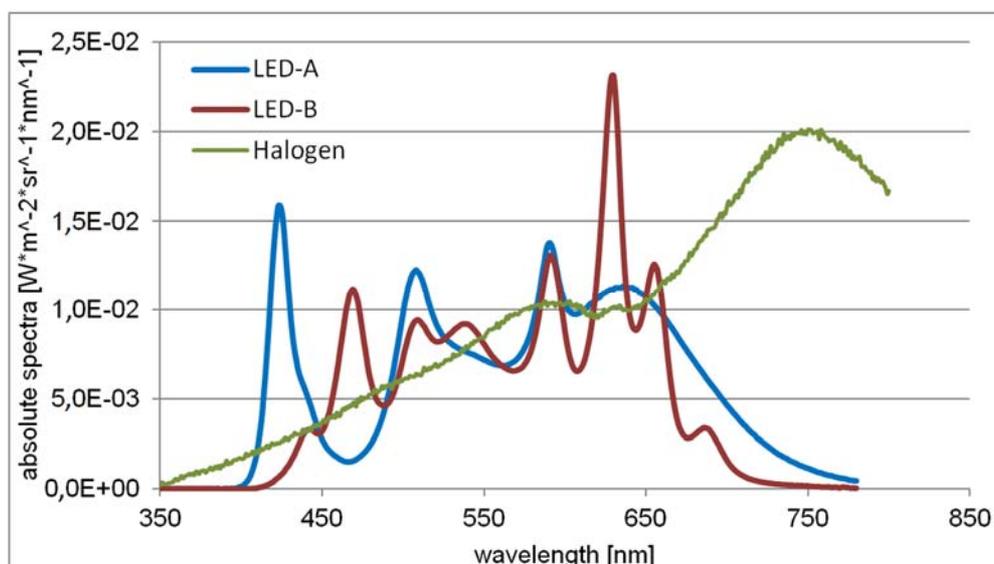


Figure 3 – Ageing spectra

The test lights (Figure 3) had high colour rendering index ( $CRI R_a \geq 88$ ), high colour fidelity and gamut area index ( $R_f \geq 79$  and  $R_g \geq 97$ ) according to IES TM-30-15 (IES, 2015) and the correlated colour temperature was 3700 K in both cases. Furthermore, for all three ageing spectra the illuminance level was set to 3000 lx.

Table 1 – Parameters of the ageing spectra

	CCT [K]	$E_v$ [lx]	$R_a$	$R_f$	$R_g$	$d_{uv}$	$DI$	$t_s$ [hours]
Booth – LED A	3677	2992	92	79,9	106,4	-0,0002	0,181	1146
Booth – LED B	3655	2982	88	84,5	97,9	0,0008	0,138	1520
Booth - Halogen	3743	2976	93	96,2	102,8	-0,0054	0,174	3532

The main difference between the two LED spectra was the spectral content below 500 nm. The “LED A” ageing spectrum included the short wavelength LED channel having a peak wavelength of 420 nm, while “LED B” contained a higher wavelength LED channel having its peak wavelength at 460 nm. The halogen spectrum in contrast had a higher content in the infrared domain. The spectra had been chosen in order to observe the effects of visible light on the photodegradation processes as well as to determine whether the spectrum with short wavelength blue LED – which is expected to be more damaging (Hattori et al. 2012) – causes more significant changes on the surface of the paint material and in the chemical structure of the paint.

Prior to the experiments, the uniformity of illumination was measured in all of the three ageing booths. The spectroradiometer used in the process was placed on the points occupied by the samples. In all three cases the uniformity of illumination was at least 0,98. In Table 1 the parameters of the ageing spectra – measured in the ageing booths – are summarized, including Damage Index ( $DI$ ), and the critical duration of exposure ( $t_s$ ) according to CIE 157:2004.

The light booths were placed in an air-conditioned laboratory room (temperature:  $22\text{ °C} \pm 1\text{ °C}$ ). During the ageing process, the temperature and relative humidity inside the ageing chambers was continuously monitored. During the ageing temperature was  $25\text{ °C} \pm 3\text{ °C}$  and relative humidity was 15% RH to 30% RH inside the lighting chambers.

## 2.3 Colour change detection

### 2.4 Ultraviolet – Visible – Near Infrared spectrophotometry (UV/Vis/NIR)

The measurement of the samples had been conducted after 1250 hours, 2400 hours, 3300 hours and 5000 hours of light exposure with a high precision spectrophotometer, using a custom-made positioning template to support the accurate repositioning of the samples for each measurement.

The samples were measured in multiple positions with the smallest (7 mm diameter) port plate, in standard diffuse/8° geometry. The spectrophotometer had been set to specular component excluded measurement configuration because of the matte surface of the samples. The instrument had been recalibrated to the white calibration tile between each colour series. Spectral reflectance data had been measured between 350 nm and 1050 nm, and the results were expressed as CIE  $L^* a^* b^*$  coordinates under D65 illuminant using the 2° standard observer.

#### 2.4.1 Statistical analysis applied on reflectance measurements results

In order to examine the measurement results more deeply and to investigate the relationship among the variables data were analysed by statistical methods as well. Mainly variance analysis (ANOVA) was used to determine the effects of a single factor. The effect of ageing period, binding material, lighting spectrum, and the type of paint sample was investigated.

## 2.5 Measurement of chemical stability

### 2.5.1 Stability of the organic part of the samples

For determining the chemical stability of the organic component in the prepared samples, Pyrolysis Gas Chromatography / Mass Spectrometry (Py-GC/MS), also in Thermally assisted Hydrolysis and Methylation mode (THM-GC/MS) were performed on the unaged, the 2400 hours and the 5000 hours aged samples. The pyrolyzer PY-2020iD (Frontier Lab, Japan) combined with a GCMS-QP2010 Plus (Shimadzu, Japan) was employed. The GC/MS unit was equipped with a capillary column (30 m length, 0,25 mm internal diameter, 0,25  $\mu$ m film thickness) using bonded and highly cross-linked 5% diphenyl / 95% dimethyl siloxane. The capillary column was connected with a deactivated silica pre-column (5 m length, 0,32 mm internal diameter). NIST 05 and NIST 05s Library of Mass Spectra were available for the identification of the compounds. Additionally, the Fourier Transform Infrared Spectroscopy analyses in Attenuated Total Reflection (FTIR-ATR) mode were carried out, equipped with a mercury cadmium telluride (MCT) detector and a germanium crystal. Spectra were acquired in the range between 4000  $\text{cm}^{-1}$  and 370  $\text{cm}^{-1}$  performing 64 scans with a resolution of 4  $\text{cm}^{-1}$ .

### 2.5.2 Stability of the inorganic part of the samples

For this investigation, the FTIR-ATR technique was used in the same configuration as for the organic part, with the addition of  $\mu$ -Raman spectroscopy. For this purpose, a confocal  $\mu$ -Raman system was used, equipped with three different laser sources: 532 nm, 632,8 nm and 785 nm and with three dielectric long pass edge filters for the rejection of the laser excitation lines. The confocal microscope was coupled to a 460 nm focal length spectrograph equipped with four different gratings (300 gr/mm, 600 gr/mm, 1200 gr/mm, 1800 gr/mm). The Raman signal was detected by a CCD detector (1024 x 256 pixels resolution, Peltier cooled to -70°C).

## 3 Results and discussion

### 3.1 Ultraviolet – Visible – Near Infrared spectrophotometry (UV/Vis/NIR)

The three lighting groups reached different irradiation doses at each period, but all three groups reached the critical threshold after the 5000 hours period. At this measurement, the samples aged under LED-A reached 439% of the critical threshold dose, in case of LED-B 330%, and 139% using the halogen lamps. Some pigment-binder combinations had shown visible changes after the ageing, but after the 5000 hours measurement all samples could be considered stable based on the reflectance measurements.

According to the measurements, pigments combined with linseed oil were the least stable – mainly due to the nature of this binding material. PB29 (ultramarine blue) – linseed oil samples showed the largest sensitivity to light. The sample aged under the LED-A spectrum shifted in colour towards blue and red ( $+a^*$ ,  $-b^*$ ). The average change was 5,32 CIELAB  $\Delta E_{ab}^*$  units in case of this sample. In case of the halogen sample the colour changed in the same direction with an average CIELAB  $\Delta E_{ab}^*$  of 4,47. In case of LED-B the direction of the change was opposite, and the magnitude was 4,9 CIELAB  $\Delta E_{ab}^*$  units. For PG18 (viridian) – linseed oil combination the halogen spectrum proved to be the most harmful. In this case the colour shift was 3,65 CIELAB  $\Delta E_{ab}^*$  units. In case of LED-A ageing of this sample  $\Delta E_{ab}^*$  was 1,32 CIELAB  $\Delta E_{ab}^*$  units. The LED-B spectrum was the more damaging ( $\Delta E_{ab}^* = 2,79$ ) than LED-A. PY37 (cadmium yellow) samples with linseed oil were slightly sensitive to LED-B, ( $\Delta E_{ab}^* = 1,85$ ) but the difference between the three samples was not significant. In contrary to the other samples, PR108 (cadmium red) samples combined with any of the binding materials were stable.

### 3.1.1.1 Statistical analyses applied to reflectance measurements: ageing period

At first, the connection between the CIELAB  $\Delta E$  colour change and the ageing period was investigated using variance analysis. This test proved a significant relationship between these variables (correlation coefficient:  $r=0,616$  and significance level:  $p<0,05$ ). Furthermore, it showed that the colour change slowed down during the ageing process. Based on the results, the biggest change took place until the 2400 hours of ageing period (Figure 4).

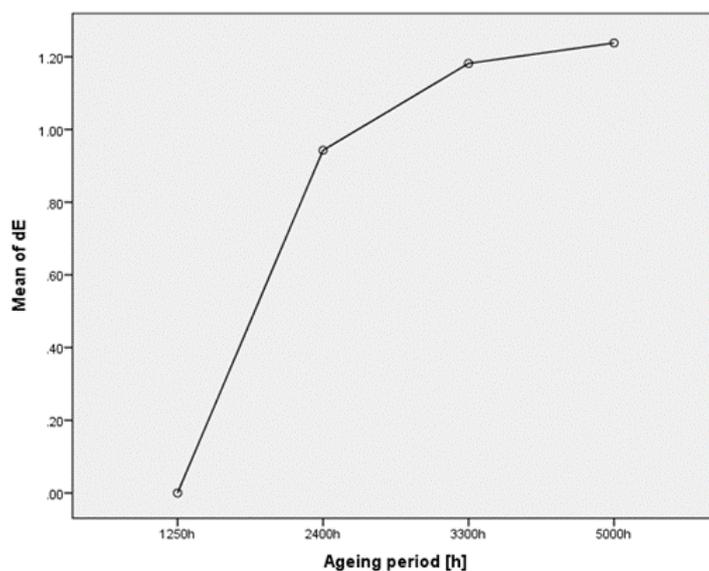
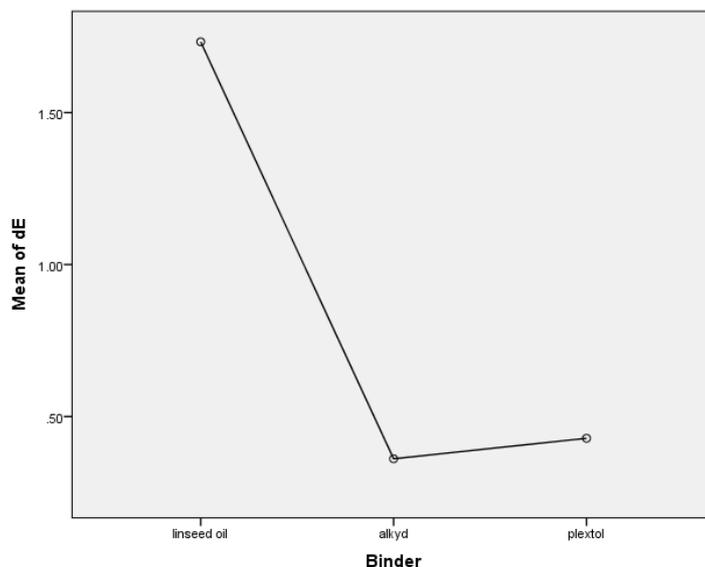


Figure 4 – Correlation between colour change and ageing period

### 3.1.1.2 Statistical analyses applied to reflectance measurements: binding material

According to the variance analysis, the type of binder plays a significant role ( $r=-0,301$  and  $p<0,05$ ) in colour change. Linseed oil shows the largest change in colour compared to the other two binding materials (alkyd and plectol) (Figure 5). The inorganic pigments can be considered stable in combination with alkyd and plectol. On the other hand, but significant changes in colour are shown when the pigments were combined with linseed oil.



**Figure 5 – Correlation between colour change and binding material**

### 3.1.1.3 Statistical analyses applied to reflectance measurements: lighting spectrum

Based on the statistical results there is no significant relationship between the variables of  $\Delta E$  colour change and lighting spectrum as well as between  $\Delta L^*$  lightness and lighting spectrum, because the significance level in these cases is greater than 0,05. Accordingly, the spectrum of light does not affect the degree of overall colour change ( $\Delta E$ ). In contrast, there is a weak ( $r < 0,1$ ) but significant relationship between the colour shift along the colour axes (CIELAB  $a^*$ - $b^*$ ) and the lighting spectrum. Based on these results the colour shift along the colour axes is wavelength dependent. More precisely, it is possible to state that the light source causes more changes along the yellow-blue axis, in which the blue wavelength component dominates, while along the red-green axis the light source causes a bigger change, in which red content dominates.

### 3.1.1.4 Statistical analyses applied to reflectance measurements: paint samples

The type of paint sample plays a significant role ( $r=0,067$  and  $p < 0,05$ ) in the degree of colour shift as well. The relationship between these variables is significant in all cases. In general samples containing the ultramarine blue pigment, and binders without pigment show the greatest colour shift (Figure 6).

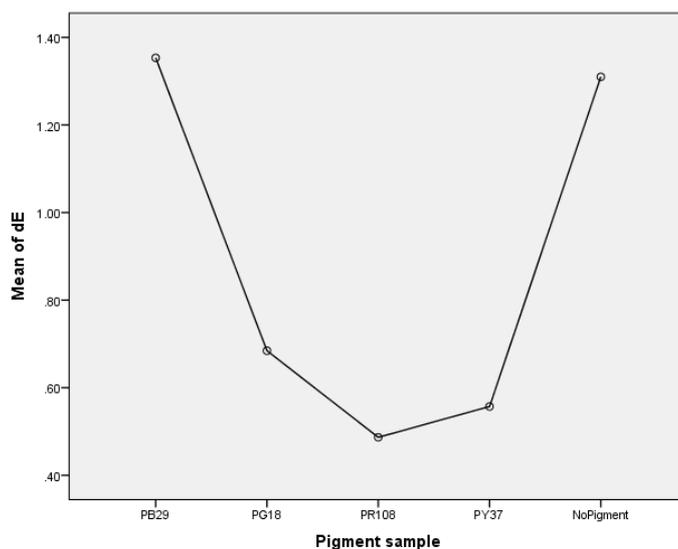


Figure 6 – Correlation between colour change and pigment type

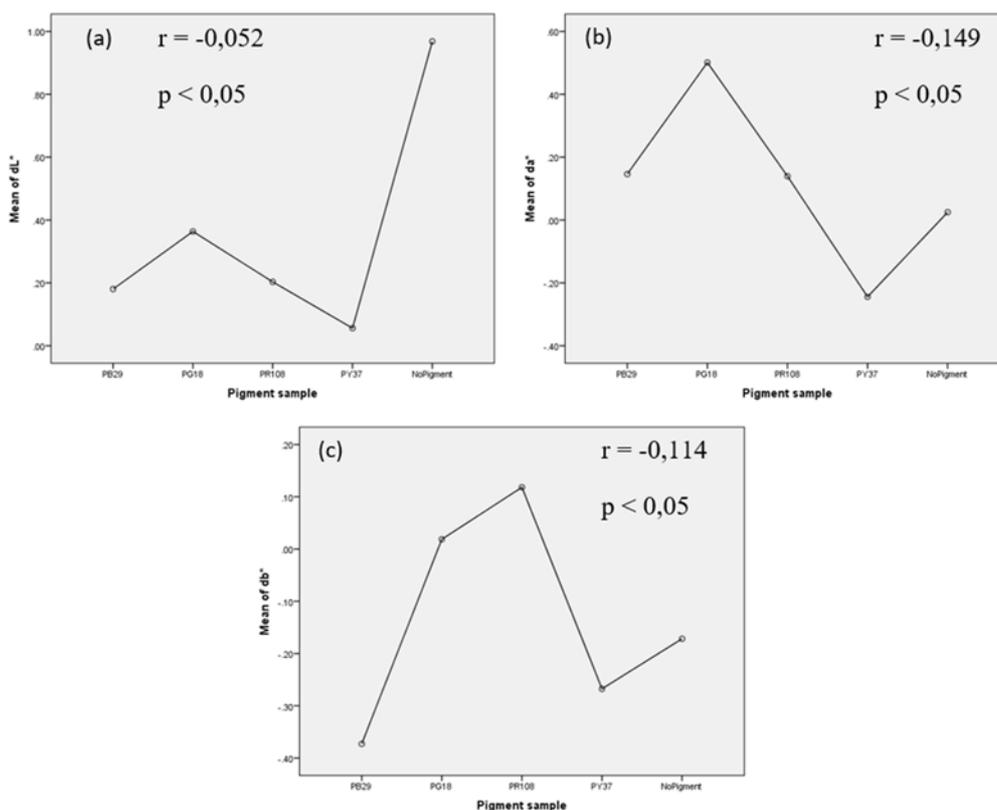


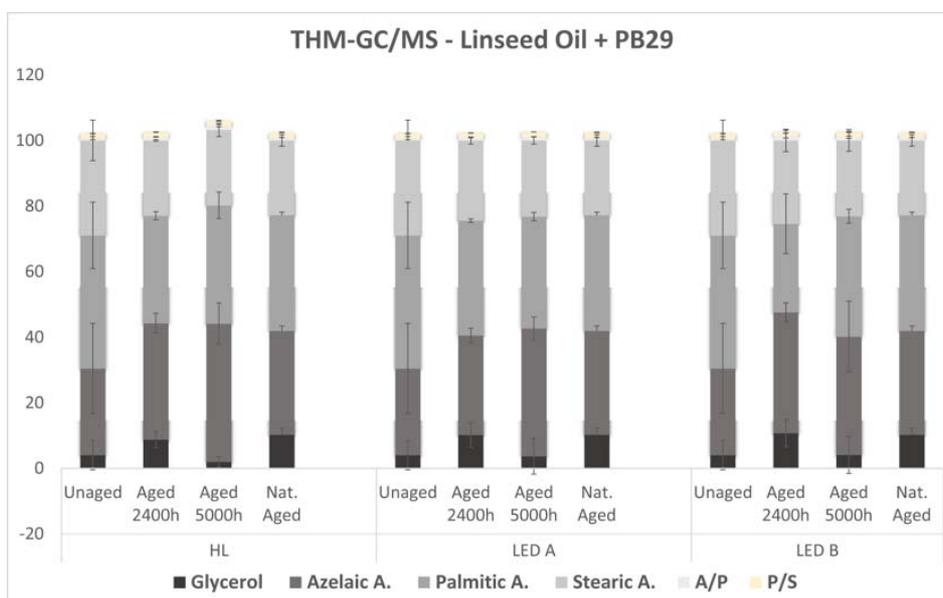
Figure 7 – Correlation between colour change and pigment type a) along CIELAB  $L^*$  axis, b) along CIELAB  $a^*$  axis, c) along CIELAB  $b^*$  axis

Examining the colour changes along the CIELAB axes (Figure 7), it can be concluded that the colour shift along the colour axes depends on the colour of the sample: along the yellow-blue axis, the pigment samples show bigger changes which are yellow or blue, while along the red-green axis the pigment samples show bigger changes which are red or green.

## 3.2 Chemical stability of the samples

### 3.3 Organic part

It was possible to study the extent of photo-oxidation with the obtained Py-GC/MS and THM-GC/MS results, based on the peak area percentage values (average and standard deviation) of the main pyrolysis products of each type of analysed unaged, 2400 h and 5000 h aged binder samples. The methyl methacrylate (MMA), n-butyl acrylate (nBA), and sum of the oligomers ( $\Sigma O$ ) were considered for the acrylic binder, while glycerol, azelaic acid (A), palmitic acid (P), stearic acid, A/P, and P/S for the linseed oil and pentaerythritol (Ph), benzoic acid, azelaic acid (A), palmitic acid (P), stearic acid (S), A/P, P/S, Ph/P, Ph/S, Ph/A for the alkyd binder. The most notable chemical differences were shown in case of the linseed oil binder, especially when mixed with the PB29 (ultramarine blue) pigment. Figure 8 shows the content of the dicarboxylic azelaic acid which is formed due to the oxidation, cross-linking and chaining scissions of unsaturated fatty acids portion, increased between 5%-10% after 5000 hours under the three different ageing spectra. The results are on the other hand comparable to the results under natural ageing conditions.



**Figure 8 – Average peak area percentage and standard deviation of the main chemical components of the linseed oil binder mixed with PB29 pigment (HL: halogen lamp, Nat. aged: naturally aged)**

In the samples with acrylic and alkyd binders no significant differences could be found.

Enrichment of pigment on the surface of the paint film as a consequence of photo-oxidation had been investigated as well. This result had been obtained by the semi-quantitative evaluation of the FTIR-ATR results. The integrated peak area ratios (average, standard deviation) between meaningful IR bands of each binder (B) and pigment (P) were the following: Acrylic: C=O at  $1726\text{ cm}^{-1}$ , CH between  $2900\text{ cm}^{-1}$ - $2800\text{ cm}^{-1}$ , Alkyd: C=O at  $1721\text{ cm}^{-1}$ , C-O-C at  $1259\text{ cm}^{-1}$ , Linseed oil: C=O at  $1736\text{ cm}^{-1}$ , CH between  $2900\text{ cm}^{-1}$ - $2800\text{ cm}^{-1}$ , PG18: Metal-oxides between  $583\text{ cm}^{-1}$ - $456\text{ cm}^{-1}$ , PB29: Al,SiO<sub>4</sub> between  $775\text{ cm}^{-1}$ - $610\text{ cm}^{-1}$ . Since the cadmium red and yellow pigments are not infrared active, the B/P values of the paints based on those two pigments could not be obtained. The carbonyl C=O band as fundamental chemical bond part of the chemical structure of the binders had been considered because of its involvement in the photo-oxidation reactions thus suggesting the possible type of chemical reactions taking place during the exposure under the lighting systems.

In accordance with the Py-GC/MS results, the most significant changes in terms of result values using the semi-quantitative approach was shown by the linseed oil mixed with the ultramarine blue PB29 pigment. A slight decrease of C=O/P and CH/P in the PB29 linseed oil mock-ups after 5000 hours of exposure under the three different illuminants (max and min

standard deviations: 0,51 and 0,04) indicates a relative enrichment of the pigment on the surface of the paint film (Figure 9).

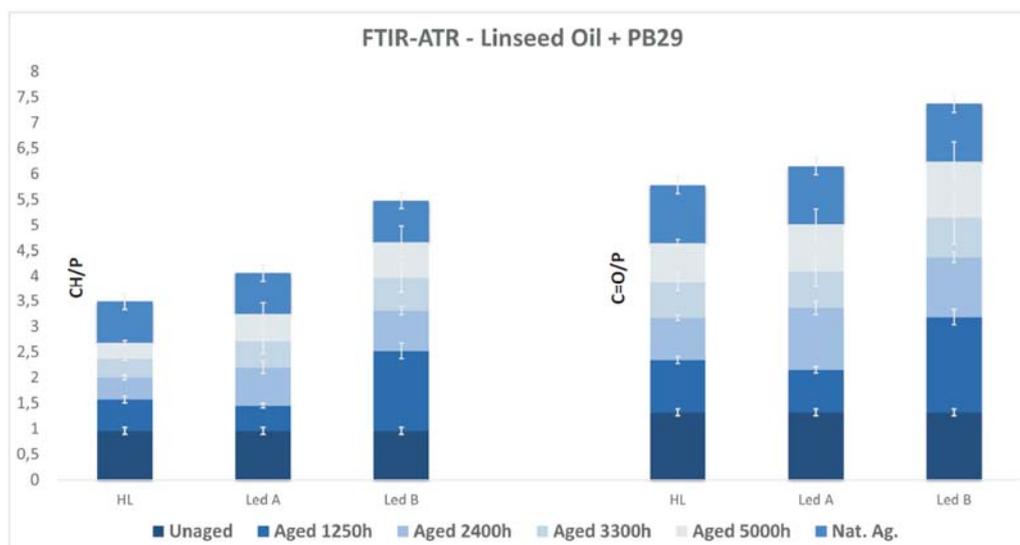


Figure 9 – Decrease of C=O/P and CH/P in the PB29 linseed oil mock-ups after 5000 hours of exposure

### 3.4 Inorganic part

$\mu$ -Raman measurements on the mock-ups determined the high stability of the selected inorganic pigments in respect to the organic binders. Similarly to the assessment of the FTIR-ATR results, semi-quantitative evaluation of the data was also performed with the calculation of the peak area percentage ratios (average and standard deviation) between meaningful Raman bands of each pigment such as blue chromophores  $S_3^-$  ( $552\text{ cm}^{-1}$ ) / yellow chromophore  $S_2^-$  ( $590\text{ cm}^{-1}$ ) for the ultramarine blue PB29, CdSe ( $290\text{ cm}^{-1}$ ) / CdS ( $196\text{ cm}^{-1}$ ) for the cadmium red PR108, and CdS 2LO ( $600\text{ cm}^{-1}$ ) / CdS 1LO ( $300\text{ cm}^{-1}$ ) for cadmium yellow PY37.

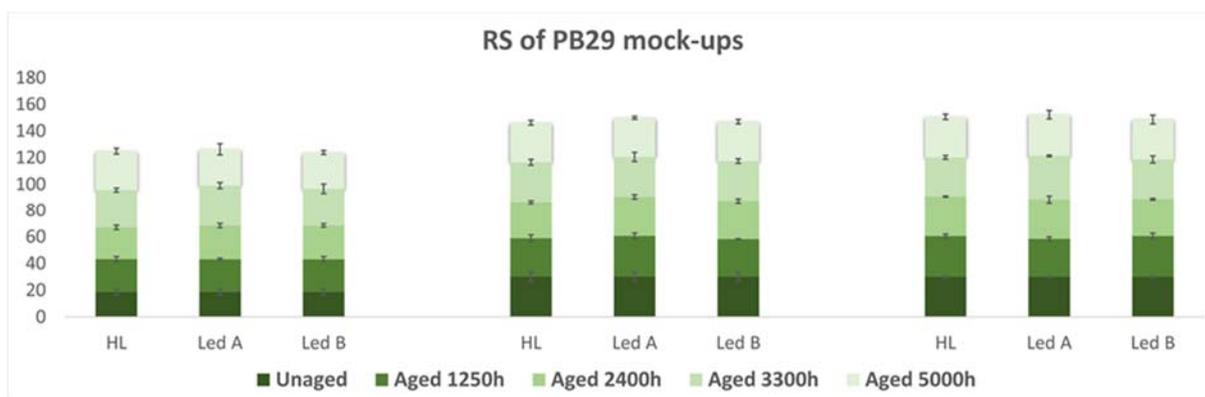


Figure 10 –  $\mu$ -Raman Spectroscopy (RS) results: Averaged values of the integrated peak areas and standard deviation of  $S_3^-/S_2^-$  for linseed oil +ultramarine blue samples before and after ageing under the 3 test illuminants (HL: halogen lamp).

No relevant changes in pigments, nor binders could be shown in the samples with acrylic and alkyd binders by  $\mu$ -Raman spectroscopy. The calculated ratios did not show significant differences between unaged and aged samples. Only for the linseed oil sample containing ultramarine blue had shown some differences between unaged and aged spectra suggesting an interaction between binder and pigment. Figure 10 depicts the peak ratios of the  $S_3^-$  and  $S_2^-$  chromophores of the PB29, which decrease in the linseed oil mock-ups in contrast to the acrylic and alkyd samples. After 5000 hours of exposure under the three illuminants (max and

min standard deviation: 3,42 – 0,57). This proves that the linseed oil binder influences the Raman signal intensity of the ultramarine blue pigment regardless the high stability of the pigment. The investigated linseed oil samples gave Raman spectra with higher noise than the paints with other binders. Namely the increase of the ratio of the integrated peaks of  $S_3^-$  and  $S_2^-$  could be related to a decreasing of the noise with ageing.

#### 4 Conclusion

Effects of LED illumination on painting materials had been investigated by combining chemical analysis and colorimetric investigations. The results of the two methods harmonize and show the background of colour changes of the selected paint samples. Among all specimens the ultramarine blue pigment (PB29) combined with linseed oil showed to be the most sensitive towards the light spectra used in the ageing process. This combination of pigment and binder showed the highest colour shift, and accordingly the result of the Py-GC/MS highlighted the greatest increase in forming dicarboxylic azelaic acid during the oxidation process. Additionally, based on the FTIR-ATR results the slightest decrease of the ratio value between the carbonyl IR band of the binder and the  $Al_2SiO_5$  IR band of the ultramarine blue indicated a relative enrichment of the pigment at the surface, while a photo-oxidative degradation processes occurred on the organic part of the sample. In case of the inorganic pigments, the  $\mu$ -Raman did not show significant differences between the unaged and aged paint samples, proving the high stability of the selected pigments. Based on the final ageing period – at 5000-hours – the results obtained with UV/Vis/NIR showed a slight change in colour, mostly in cases where linseed oil binder was used. The largest difference could be measured in case of the PB29 whereasthe CIELAB  $\Delta E_{ab}^*$  was more than four units for all samples. It was the largest in case of the sample aged under LED-A – more than five units. The linseed oil mixed – PG18 (chromium oxide green hydrated) combination showed the largest change when exposed to the halogen lamp, while linseed oil – PY37 (cadmium yellow) when aged with LED-B. PR108 (cadmium red) pigment could be considered stable in every case.

#### Acknowledgement

The authors gratefully acknowledge the support of their research by the Austrian Agency for International Cooperation in Education and Research (OeAD-GmbH) and the Hungarian National Research, Development and Innovation Office (grant number: TÉT\_15-1-2016-0017).

#### References

- CIE 1991. CIE 89-1991. *Technical Collection 1990: 89/3 On the Deterioration of Exhibited Museum Objects by Optical Radiation*. Vienna: CIE.
- CIE 2004. CIE 157:2004. *Control of Damage to Museum Objects by Optical Radiation*. Vienna: CIE
- HATTORI, H, YOSHIZUMI, K, CREWS, P. 2012. Wavelength sensitivity of AATCC Blue wool lightfastness standards under light radiation. *Dyes and Pigments*, 92(3), 936-941.
- IES 2015. IES TM-30-15. *IES method for evaluating light source color rendition*. New York: IES.