Colour measurements intercomparison of disinfected by irradiation polychromed wooden objects

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Abstract

Gamma irradiation treatment is an efficient mean of mass disinfection of wooden objects contaminated by fungi and insects. Among the more or less significant changes in the physico-chemical properties of materials which could be induced by gamma irradiation, colour changes of polychromed wood are often feared by the conservators in charge of such collections and have to be evaluated objectively and precisely using colour measuring instruments. These instruments come in many configurations, so the inter-instrument agreement is very important. The aims of this work are to check the inter-instrument agreement between two reflectance spectrophotometers and evaluate the colour stability over time for a set of un- and irradiated painted wooden panels.

1. INTRODUCTION

The most important species involved in the biodeterioration of wooden objects are fungi and insects. Gamma irradiation is a treatment aiming in prevention from these biodeteriorating organisms and remediation (curing) of infected objects. Applied absorbed doses are chosen according to radio-resistance of the species implied in biodeterioration, ranging from 500 Gy (enough to kill larvae and prevent the emergence of adult insects) to about 10 kGy (at which most of the fungi are killed) [1]. The effects on wooden material at these doses are known to be acceptable for the community involved in conservation of cultural heritage artefacts.

The case of painted wooden supports has to be studied separately. Polychrome layers are subdivided in a preparation layer and a paint layer, the chemical composition of which varies according to the mode and the period of painting. For the historical period in European regions, the preparation layer is usually made with lime or gypsum with addition of animal or vegetal glue. On this smooth surface several layers of colour are present, which consist of pigments mixed with binders of oil or distemper (egg or glue). The surfaces could also be covered with a thin, translucent protective varnish.

Because of more or less significant changes in the physical and chemical properties of materials which could be induced by gamma irradiation, the unlikely but still possible colour changes of polychromed wood have to be evaluated. Perceptions of colour being subjective and physiologically dependant, colour measuring instruments (colorimeters and spectrophotometers) must be used to quantify these potential colour differences. There are six parameters that affect the colour measurement: colour scale, illuminant, standard observer, the instrument itself (type, geometry, and standardization mode), the way of presenting the sample to the instrument, and finally the method of preparing the samples themselves. If one or more of these parameters is changed, the colour values are also changed. The

first three of these criteria have to be chosen according standardization. Spectrophotometers come in many sizes, shapes, geometries, and configurations, so inter-instrument agreement is a complex topic, but it theoretically belongs to standardization. As a matter of fact, to obtain the best inter-instrument agreement in terms of absolute colour values, one has to use the same model of instrument from the same manufacturer with all the six parameters matching. However, instruments of the same geometry should agree on difference values from a physical standard, even if they do not agree exactly on absolute colour values [2].

The aims of this work are to:

- check the inter-instrument agreement between two reflectance spectrophotometers: HunterLab Miniscan XE Plus (HL) and Konica Minolta CM-508i (CM);
- evaluate the colour stability over 1 year for a set of un- and irradiated painted wooden panels.

2. MATERIALS AND METHODS

Two sets of samples were used in this work: (A) for the inter-comparison of the two spectrophotometers and (B) for checking the colour stability over time for un- and irradiated painted wooden samples.

Samples (A), prepared at ARC-Nucléart (France), are small pieces of wood covered by a preparation layer (chalk in mixture with rabbit skin glue) on which binders (3, 6, 9, and 12 layers) or pigments in mixture with poppy seed oil are painted. These samples were prepared in two series: one unirradiated, used as a reference and the other was gamma irradiated at 200 kGy (approximately twenty times the usual dose for eradication of fungi). As the uniformity of the samples is very important in colour measurement comparisons, samples (A) were visually inspected (for cracks, traces of brush strokes etc.) and arbitrary grouped in three classes according to their uniformity: good, medium and bad. Samples (B), prepared by Conservation-Restoration Department of National University of Arts (Romania), consist of small pieces of wood covered by a ground layer (chalk in mixture with rabbit skin glue) and pigments mixed with tempera (aqueous solution of yolk egg and water). Half of every sample was additionally varnished with Dammar- this is indicated by "+v". Samples (B) were prepared in three series: one unirradiated, used as a reference, and two irradiated at 11 kGy but using two dose ratios: 35 Gy/min (indicated by "d") and 245 Gy/min ("D").

Reflectance spectrometry was used for colour measurements of these opaque ample. The results of measurements are reported in both CIE L*a*b* and CIE L*C*h and presented as differences between sample and its corresponding reference [3]. Total colour differences dE* being small, dE CMC formula was also used with a lightness to chroma ratio of 2:1. In Table 1 are presented the characteristics of the two colour measuring instruments used in the inter-comparison. The two spectrophotometers differ in: spectral resolution, reflectance range and diameter of measuring beam / view area; they should agree on difference values.

Table 1: Characteristics of reflectance spectrophotometers

Instrument	Miniscan XE Plus (HL)	CM-508i (CM)
Manufacturer	Hunter Associates Laboratory, Inc.	Konica Minolta Sensing, Inc.
Colour scale	CIE L*a*b* and CIE L*C*h	CIE L*a*b* and CIE L*C*h
Illuminant	D_{65}	D_{65}
Standard observer	10°	10°
Geometry of measurement	d/8°	d/8°
Spectral range	400 – 700 nm	400 – 700 nm
Spectral resolution	10 nm	20 nm
Reflectance range	0 – 150 %	0 – 175 %
Port diameter / view diameter	6.0 / 4.0 mm	11.0 / 8.0 mm

3. RESULTS AND DISCUTION

3.1. Intercomparison

Samples (A) were measured with CM at ARC-Nucléart and with HL at IFIN-HH; time interval between the two series of measurements is two weeks. The results are presented in Table 2 as differences between colour values obtained from irradiated samples (200 kGy) and their corresponding references.

For samples prepared with binders (rabbit skin glue, linseed oil and poppy seed oil), without pigments, the agreement was good. In this paper are presented only the samples with 12 layers of binders; for samples with a lower number of layers the agreement is much better. The highest disagreement, only quantitative, is for lightness (L*): CM indicates a higher difference in L*. Regarding the effect of gamma irradiation, there are small colour differences; even in the case of rabbit skin glue, the main component of colour difference is from chroma- considering 12 layers of binder and 200 kGy, this difference is still acceptable, although this dose is 20 times the reference dose for disinfections.

In the case of samples prepared with different pigments in mixture with poppy seed oil, the agreement between the two spectrophotometers is depending on the uniformity of the sample. One can observe that even for the samples of bad uniformity (Solferino lake and cadmium red) for which the disagreement (considering the colour differences on components) is not only quantitative, but also qualitative, the total colour differences (dE* and dE CMC) are very close.

3.2. Colour stability over time

Colour stability over time for samples (B) was evaluated using HL. The interval of time between the two series of measurements is one year. The results are presented in Table 3; values obtained in the last year were used as references.

Colour shift in time is insignificant for samples prepared with mars red and chrome yellow. The colour of varnished samples prepared with minium and raw Sienna was the most unstable. Irradiated samples are less stable than unirradiated ones, except unvarnished raw Sienna and mars red. This influence of irradiation is only quantitative. Colour shift over time increase with the dose ratio. Varnish does not influence the colour stability over time except samples prepared with raw Sienna where the colour shift is higher for varnished samples.

4. CONCLUSIONS

The agreement of the two intercompared spectrophotometers is depending on the uniformity of the samples, but even for samples of bad uniformity as Solferino lake the agreement is good in total colour differences values. Regarding the effect of very high doses gamma irradiation on the colour of samples (A), total colour differences are lower than 5 dE* units (i.e. small colour differences) except cobalt blue, ochre yellow, and rabbit-skin glue.
Irradiation increases the colour shift over time of samples (B) except unvarnished raw Sienna and mars red; the influence of irradiation is only quantitative. The colour shift increase with the dose ratio.

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Table 2: Colour differences for samples (A) measured with HL and CM

sample [uniformity]	instrument	dL*	da*	db*	dC*	dh	dE*	dE CMC
rabbit skin glue (12 layers) [good]	HL	-1.18	-0.19	6.35	6.33	1.10	6.46	3.61
	CM	-2.60	-0.10	6.05	6.02	1.15	6.59	3.39
linseed oil (12 layers) [good]	HL	-0.56	0.40	0.62	0.66	0.82	0.92	0.52
	CM	-2.54	0.47	0.61	0.66	-1.09	2.65	1.06
poppy seed oil (12 layers) [good]	HL	-0.17	-0.46	1.57	1.62	1.14	1.64	1.42
	CM	-1.33	-0.48	2.36	2.41	0.64	2.75	2.14
ivory black [medium]	HL	-1.51	-0.03	-0.07	0.08	-0.53	1.51	1.33
	CM	-2.01	-0.19	-1.16	0.20	192.44	2.33	2.37
silver white [medium]	HL	-1.85	-0.36	1.97	1.98	1.76	2.73	1.99
	CM	0.35	-0.55	2.74	2.75	3.86	2.82	2.88
Prussian blue [medium]	HL	-0.09	-0.54	4.39	-4.43	0.05	4.43	3.16
	CM	-1.51	-0.93	4.23	-4.32	-1.52	4.59	3.23
Brunswick blue [medium]	HL	-0.75	0.84	2.01	-2.13	2.35	2.30	1.83
	CM	-0.92	0.84	2.99	-3.10	1.04	3.24	2.44
raw umber [good]	HL	0.73	-0.33	-0.34	-0.41	1.19	0.87	0.66
	CM	0.44	-0.05	-0.33	-0.30	0.78	0.55	0.43
cadmium red [bad]	HL	-0.02	0.31	1.02	0.83	0.62	1.06	0.56
	CM	-0.26	0.20	-0.64	-0.19	-0.59	0.72	0.47
Solferino lake [bad]	HL	-2.10	-1.71	0.35	-1.50	0.76	2.73	1.24
	CM	1.81	0.86	-1.02	0.45	-1.05	2.25	1.17
cobalt blue [bad]	HL	-2.10	3.22	-4.07	3.68	4.46	5.60	2.98
	CM	-4.92	7.18	-3.49	2.68	8.96	9.38	5.37
ultramarine [bad]	HL	0.90	2.00	-3.00	3.32	1.37	3.72	1.60
	CM	0.39	5.45	-6.05	7.05	3.83	8.15	3.69
titanium white [medium]	HL	-1.60	0.26	0.76	0.76	-2.26	1.80	1.00
	CM	-1.31	-0.12	1.45	1.45	0.77	1.96	1.51
napples yellow [medium]	HL	0.82	-0.18	-1.58	-1.58	0.18	1.79	0.82
	CM	-0.66	-0.51	-3.70	-3.72	0.59	3.79	1.79
cadmium yellow (citron) [bad]	HL	-1.39	1.03	-1.92	-1.96	-0.61	2.58	0.91
	CM	-0.20	0.23	-0.20	-0.21	-0.14	0.36	0.15
cadium yellow [bad]	HL	0.54	0.31	2.85	2.70	0.67	2.92	1.14
	CM	2.01	0.75	5.09	4.91	1.05	5.52	2.10
ochre yellow [bad]	HL	4.29	-0.86	4.30	3.55	2.61	6.14	3.19
	CM	3.71	0.50	5.34	5.06	1.81	6.52	2.91

Tabel 3: Colour shift over time for samples (B)

sample	dL*	da*	db*	dC*	dh	dE*	dE CMC
raw Sienna	-1.32	-0.77	-3.30	-3.32	-0.87	3.64	1.59
raw Sienna (d)	0.47	-0.34	0.18	0.03	0.47	0.61	0.41
raw Sienna (D)	0.71	-0.76	-0.88	-1.11	0.42	1.36	0.63
raw Sienna v	3.04	1.13	3.56	3.65	1.30	4.81	2.51
raw Sienna v (d)	6.28	1.83	7.24	7.25	2.78	9.76	5.12
raw Sienna v (D)	7.18	1.33	8.37	8.01	4.22	11.11	6.19
minium	-0.29	-1.49	-1.28	-1.95	0.17	1.98	0.67
minium (d)	-1.81	-3.27	-4.84	-5.78	-0.67	6.12	2.16
minium (D)	-0.84	-3.00	-7.20	-7.31	-2.21	7.85	3.27
minium v	-0.48	-1.96	-3.09	-3.61	-0.52	3.69	1.32
minium v (d)	-1.91	-2.49	-4.74	-5.18	-1.08	5.68	2.19
minium v (D)	-2.17	-3.45	-5.91	-6.69	-1.18	7.18	2.67
mars red	0.25	-0.81	-0.69	-1.06	-0.21	1.09	0.55
mars red (d)	-0.28	-1.30	-0.82	-1.54	0.07	1.56	0.77
mars red (D)	-1.06	-1.56	-0.59	-1.62	0.74	1.98	1.07
mars red v	-0.44	-1.25	-0.60	-1.37	0.43	1.46	0.74
mars red v (d)	-0.13	-1.40	-0.82	-1.61	0.23	1.62	0.80
mars red v (D)	-0.57	-1.18	-0.57	-1.30	0.39	1.43	0.73
chrome yellow	-1.14	0.41	-1.68	-1.67	-0.27	2.07	0.69
chrome yellow (d)	-0.47	0.54	1.15	1.14	-0.37	1.35	0.49
chrome yellow (D)	-2.30	-0.80	-4.25	-4.23	0.61	4.89	1.63
chrome yellow v	-0.90	0.59	-0.21	-0.19	-0.39	1.09	0.45
chrome yellow v (d)	-1.13	-0.14	-2.27	-2.27	0.12	2.54	0.83
chrome yellow v (D)	-1.64	-1.95	-2.75	-2.70	1.42	3.74	1.49

References

1. Tiano, P.: “Biodegradation of Cultural Heritage: Decay Mechanisms and Control Methods”. http://www.arcchip.cz/w09/w09_tiano.pdf
2. HunterLab (2008): Maximizing Inter-instrument Agreement. http://www.hunterlab.com/appnotes/an06_05.pdf
3. Brainard, D.H. (2003): “Color appearance and Color Difference Specification”. In Shevell, S.K. (Ed.), “The Science of Color (2nd edition)”. Oxford UK: Elsevier.
4. ISO 105 Part J03 (2006): Calculation of colour differences