

Paintings: monitoring varnish variations and their effect on color perception. A case study.

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ABSTRACT

Color monitoring is one of the methods used for following degradation on varnish applied on paintings. Collecting colorimetric data for monitoring purposes is done effectively, rapidly, inexpensively and non-invasively. In general, colorimetric data are easy to record and read, but the variables associated with them are not always given due consideration. Starting from a specific case study, the panel painting 'Resurrection of Christ and Saints' (1568) by Giorgio Vasari in the basilica of Santa Maria Novella in Florence (Italy), an attempt was made to define a working methodology while providing suggestions for proper planning for monitoring and evaluating the acquired data. The colorimetric data were acquired using a Konica-Minolta model CM-700d colorimeter. The methodology accuracy and repeatability was assured by evaluating the repositioning operations of the instrument on the area of measurements over time, also keeping in mind possible errors induced by operators.

KEYWORDS: varnish for paintings, colorimetric measurements, spectrophotometer, Giorgio Vasari, Santa Maria Novella.

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1. Introduction

A painting is created by layers of color (pigment and binder) often protected by an outer layer of varnish. The eye perceives the image itself as formed by the varnish-paint system. Consequently, any variation in the varnish inevitably has an effect on this system, causing the color of the image to be perceived differently. The main function of varnish is fundamentally aesthetic as its presence improves the optical characteristics of the painted surface, making it glossier (decreasing the component of diffuse light), smoother and more uniform, and increasing the saturation of colors (Bestetti, 2020; Chercoles et al., 2011; de la Rie, 1992; Maines and de la Rie, 2005; Phenix, 1993). The final varnish of a polychrome work, being the outermost layer, is the one that, due to its position and nature, is exposed to the greatest degradation by external agents. The materials originally used for varnish, traditionally natural resins, change mainly due to photo-oxidative degradation caused by exposure to ultraviolet (UV) radiation and oxygen, resulting in yellowing, loss of transparency, cracking and loss of solubility (Bestetti, 2020; Stoner and Rushfield, 2012).

Non-invasive imaging and analytical techniques are of great importance in the field of preventive conservation of cultural heritage (Aldrovandi and Picollo, 2007; Pinna et al., 2009) as they can be applied on artworks by replicating measurements over time. Among the various methodologies that fall into this group, the use of devices for defining the color of surfaces, or parts of them, is very useful for monitoring the color of artworks over time to highlight any color changes. Colorimetry, in fact, is widely used in the field of art conservation. This technique is commonly used to monitor color over time and highlight color changes that may occur, for example, as a result of alteration processes or to highlight metamerism phenomena following exposure of the artwork to light with different emission spectra. It is particularly useful for monitoring cleaning and inpainting procedures on polychrome works; for measuring color before, during and after such operations (Bacci et al., 2003; Johnston-Feller, 2001; Vila and Murray, 2022).

Colorimetric measurement at several points of the artwork can be a useful indicator of the stability of the varnish-paint system and thus of the varnish itself.

Measuring the color of selected areas of a work of art is a simple operation, but there are many variables that, if not considered or approached superficially, can invalidate a planned monitoring over years. The most important of these are the following:

1. The selection of the areas for analysis over the years. This operation must take into account a series of considerations including: a) accessibility of the

artwork throughout the investigation period; b) color homogeneity of the paint layer in the area of interest; c) choice of colors particularly sensitive to variations due to the aging of the external film-forming layer; d) implementation of a method for the correct positioning of the instrumentation on the measurement areas; e) in the case of using positioning systems with reference masks, check the ease of placement before starting the measurement campaign.

2. If measuring masks are used, this operation requires a transparent material: a) stable over time, i.e. one that does not deform over the years (ideally is a sheet of Melinex[®], a high quality polyester film), and easily drillable; b) on which it is possible to mark references for the correct repositioning of the mask on the surface of the artwork and of the instrument for acquiring the measurements.
3. The measurement mode.

This paper presents the experience gained over five years of monitoring a panel painting (439.5 cm x 295 cm) by Giorgio Vasari depicting the 'Resurrection of Christ and Saints' (1568) in the basilica of Santa Maria Novella in Florence (Figs. 1 and 2).



Fig. 1. 'Resurrection of Christ and Saints' panel painting (1568) by Giorgio Vasari after restoration (photo by Claudia Gisela Reichold).



Fig. 2. Colorimetric measurements selected spots (photo by Claudia Gisela Reichold).

The artwork, on which the varnish had just been applied to finalize its restoration work, which therefore corresponded to time “zero” (T0), was deemed a perfect case study to validate the monitoring methodology of any observed color variations for the varnish-paint system. The possible causes of degradation of this system and monitoring of environmental parameters (temperature, relative humidity, pollutants, etc.) were considered not of interest in the definition of the monitoring methodology.

For the acquisition of the reflectance spectra, and the subsequent colorimetric calculation, a Konica-Minolta model CM-700d colorimeter and SpectraMagic NX software were used.

In particular, this work focuses on: a) the methodology developed to allow the repetition of measurement campaigns over time; b) acquired data processing; c) their meaning in relation to the monitoring over time of the optical properties of the varnish and the pictorial film; d) the problems associated with the implementation of these monitoring campaigns.

2. “Resurrection of Christ and Saints” (1568) by Giorgio Vasari

Giorgio Vasari was commissioned by Cosimo I de' Medici to thoroughly renovate Santa Maria Novella in Florence following the new orientations of the Counter-Reformation. As part of this immense project, he painted the “Resurrection of Christ with Saints Cosmas and Damian, John the Baptist and Andrew” for the Basilica in 1568. Unfortunately, after ca 450 years the image of the wood panel painting was difficult to “read” due to layers of environmental deposits such as black carbon from hundreds of thousands of candles in centuries, yellowed and oxidized varnishes and altered materials from “refreshing treatments”, overpaintings, etc. Therefore, as part of the long and complex restoration intervention

dictated by the conservation conditions of the work, a new respectful cleaning was deemed necessary. The severest problem was caused by previous aggressive cleaning causing the loss of original paint material which had irretrievably disfigured the image. To hide this serious damage, entire sections of the work had been covered in black oil paint, upsetting not only the chromatic values, but also the iconographic meaning and compositional spatiality. During this last restoration, after having recovered the original color fragments, the aim was to identify and rediscover the potential unity of the work; following in-depth studies and long reflections and always having Vasari's drawing as a guide and confirmation the aim of the retouching was, in tip of the brush, to gradually recover the values distorted by previous interventions, thus seeking a new balance. As reported earlier, the time at which the varnish was applied to the paint film at the conclusion of the restoration is considered the T0 of the monitoring of the varnish-paint system. In this way, chromatic values and spatiality of the precious mannerist work were restored, once again allowing a truthful and correct reading, and to enjoy its full beauty.

3. Methodology

Eight measurement areas were selected at the bottom of the panel painting. This choice was made for logistical reasons since the artwork, after its restoration, had been recollocated in its original position, in the fourth altar of the west aisle wall of the basilica (basal part of the painting placed approximately 150 cm from the floor). Since it was not possible to use scaffolding or other structures to reach the central or top areas of the painting, and for the distance imposed by the altar itself, only the basal parts of the work were considered for this study. Furthermore, the selection of the areas to be analyzed was determined by the possibility to have colors that were as homogenous as possible and with hues that were more chromatically sensitive to variations in the transparency of the varnish. This led to the choice of light color tones with blue-green and magenta-lilac shades.

Measurements were performed on: 25th January, 2019 (T0); 24th July, 2019 (T1); 13th February, 2020 (T2); 21st July, 2020 (T3); 22nd June, 2021 (T4); 15th March, 2022 (T5); 3rd April, 2023 (T6); 2nd February, 2024 (T7).

All measurements were performed by the same operators, including the positioning of both the masks and the colorimeter on the measurement points. Five measurements were acquired for each spot, assuring to reposition the instrument on the mask at each single acquisition. The instrumental parameters were set as follows: 8 mm aperture (MAV), specular component excluded (SCE) and included (SCI). It was decided to

consider the two measurement geometries in order to highlight any changes in the filmogenic layer attributable to physical changes in the film (e.g. gloss reduction over time). Colorimetric data were calculated for the 10° Supplementary Standard Observer and D65 Illuminant in the CIEL*a*b* 1976 color space. The L*, a* and b* parameters obtained from the five acquisitions for each measurement were averaged for each spot and the maximum error was also calculated to define the validity of the data obtained. Colour differences were then calculated using the CIEDE2000 colour difference formula (ΔE_{00}) (Sharma et al., 2005). The evaluation of the accuracy and repeatability of the measurements within a specific measurement campaign was made by considering the values of the maximum errors for the three colorimetric parameters. In the case of homogenous paint layer, when these errors are small (generally < 0.5), it means that the repositioning of the instrument on the mask was done with good precision. The accuracy and reproducibility of mask positioning, on the other hand, was verified by observing the trend of the color variation values over time. If this tendency presents a progressive and constant trend over time, without marked fluctuations, it can be assumed that this operation has been performed correctly and is therefore reproducible.

4. Results

The results obtained at the end of the first five years of monitoring are presented and discussed below. Particular attention has been given to their evaluation in relation to the methodology of acquisition of colorimetric data on the artwork.

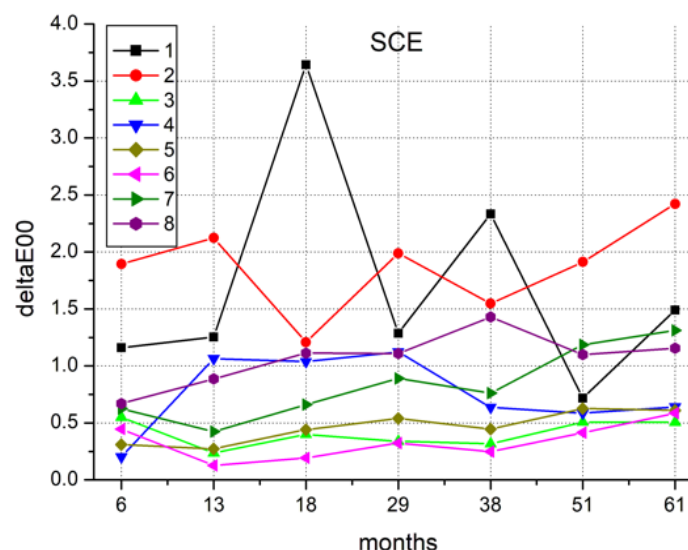


Fig. 3. Trend of ΔE_{00} values of measurements in SCE mode for selected areas.

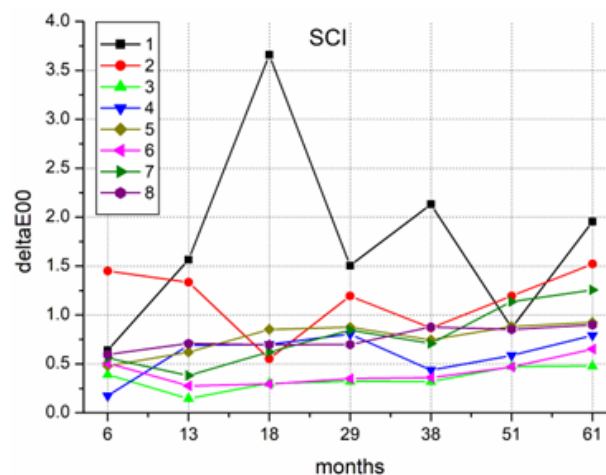


Fig. 4. Trend of ΔE_{00} values of measurements in SCI mode for selected areas.

From the data shown in Table 1, it is evident that measurement points 3-8 do not show appreciable changes over the time period considered. In fact, they generally present values of $\Delta E_{00} < 1$, reaching a maximum value of ΔE_{00} around 1.5. Furthermore, the trend of ΔE_{00} values during monitoring is constant without marked fluctuations or trends. For these measurement zones, observing the average data and maximum errors for the three colorimetric parameters of each measurement set, it can be argued that the positioning of both the instrument and the masks were performed optimally. In fact, the maximum errors for each measurement set for the three colorimetric parameters are overall low (< 0.5), and the color variation values over time show a rather regular upward trend (Table 1). This trend indicates a slight variation in the color values of the film-forming layer, even if to date it is not visually perceptible.

With regard to measurement points 1 and 2, the values found are difficult to interpret. In fact, the ΔE_{00} values calculated for the spot 1 show a strong variation during monitoring with a fluctuating trend. As shown in Figures 3 and 4, the SCE mode ΔE_{00} values are at T1 slightly above 1, then rise at T3 with $\Delta E_{00} > 3$, then return at T4 to values similar ($\Delta E_{00} = 1.29$) to the initial ones, rise abruptly at T5 ($\Delta E_{00} = 2.33$), then fall at T6 to values below those measured at T1 ($\Delta E_{00} = 0.72$) and finally rise twice as high at T7 ($\Delta E_{00} = 1.49$). The same fluctuating trend was recorded for the measurements in SCI mode, although in this case the initial differences were smaller than those observed in SCE mode. This same behavior is also observed in Table 2, where the L*, a* and b* values over time show fluctuating trends, indicating a mask repositioning procedure that is not always correct on the area of interest. In fact, even on surfaces with relatively uniform colors, small movements of the measurement area can lead to different colorimetric values.

For measurement zones 1 and 2, when observing the maximum errors for each colorimetric parameter in each set of measurements, it can be seen that they are > 0.5

(this is evident in the measurement at T0). This indicates that the repositioning of the instrument on the mask may not have been done with good precision.

			ΔE_{00}							
difference	months		1	2	3	4	5	6	7	8
T1 - T0	6	SCI	0.64	1.45	0.39	0.17	0.48	0.51	0.56	0.60
		SCE	1.16	1.90	0.55	0.20	0.31	0.45	0.62	0.67
T2 - T0	13	SCI	1.56	1.34	0.15	0.69	0.62	0.28	0.38	0.71
		SCE	1.25	2.12	0.23	1.06	0.27	0.13	0.42	0.89
T3 - T0	18	SCI	3.66	0.55	0.30	0.70	0.85	0.29	0.62	0.70
		SCE	3.64	1.21	0.40	1.04	0.44	0.19	0.66	1.11
T4 - T0	29	SCI	1.50	1.19	0.32	0.81	0.88	0.35	0.85	0.70
		SCE	1.29	1.99	0.34	1.12	0.54	0.32	0.89	1.11
T5 - T0	38	SCI	2.13	0.87	0.32	0.44	0.75	0.36	0.71	0.88
		SCE	2.33	1.55	0.32	0.64	0.45	0.25	0.76	1.43
T6 - T0	51	SCI	0.87	1.19	0.47	0.59	0.88	0.47	1.14	0.85
		SCE	0.72	1.91	0.51	0.59	0.63	0.42	1.19	1.10
T7 - T0	61	SCI	1.95	1.52	0.48	0.79	0.92	0.65	1.26	0.90
		SCE	1.49	2.42	0.51	0.64	0.61	0.59	1.31	1.16

Table 1. Color difference (ΔE_{00}) of the eight measured spots.

	T1 - T0		T2 - T0		T3 - T0		T4 - T0		T5 - T0		T6 - T0		T7 - T0	
	SCI	SCE	SCI	SCE	SCI	SCE	SCI	SCE	SCI	SCE	SCI	SCE	SCI	SCE
	Spot 1													
ΔL	0.24	0.96	-1.68	-1.26	-3.93	-3.71	-1.67	-1.34	-2.28	-2.34	-0.75	-0.21	-2.05	-1.39
max error	1.56	1.50	1.67	1.67	1.25	1.37	1.17	1.17	1.16	1.09	1.43	1.13	1.22	1.41
Δa	-0.59	-0.81	0.61	0.56	1.34	1.44	0.32	0.32	0.79	1.01	-0.06	-0.22	0.52	0.36
max error	0.70	0.77	0.80	0.90	0.56	0.71	0.52	0.62	0.49	0.61	0.68	0.61	0.53	0.62
Δb	0.12	-0.01	0.37	0.42	0.4	0.52	0.49	0.53	0.65	0.79	0.71	0.76	1.01	1.07
max error	0.08	0.11	0.08	0.16	0.06	0.13	0.04	0.11	0.05	0.14	0.05	0.12	0.06	0.11
	Spot 2													
ΔL	1.50	1.84	1.38	2.09	0.50	1.14	1.21	1.93	0.78	1.50	1.24	1.89	1.47	2.31
max error	2.03	1.77	1.27	0.94	1.25	0.89	1.34	0.93	1.23	0.87	1.22	0.81	1.22	0.89
Δa	-0.26	-0.36	-0.25	-0.36	-0.25	-0.38	-0.19	-0.34	-0.23	-0.35	-0.02	-0.11	-0.26	-0.41
max error	0.17	0.18	0.17	0.18	0.18	0.20	0.19	0.16	0.17	0.18	0.17	0.17	0.17	0.17
Δb	0.10	0.28	0.04	0.14	-0.18	-0.12	0.27	0.36	0.39	0.04	0.31	0.43	0.59	0.67
max error	0.91	0.67	0.52	0.30	0.54	0.31	0.53	0.28	0.89	0.26	0.49	0.23	0.48	0.26

Table 2. Differences of color values (ΔL^* , Δa^* , Δb^*) over time and sum of maximum deviations for measurement points 1 and 2.

5. Conclusions

In general, colorimetric measurements are particularly useful for following the cleaning and inpainting procedures on polychrome works, as they make it possible to monitor the color over time and reveal any chromatic variations in the pictorial film. The measurement methodology is quick and easy to apply, but has numerous variables that must be taken into account in order to carry out reliable and repeatable measurements. It is important to take into account errors associated with the methodology itself and those associated to the operator carrying out the measurement.

In terms of repositioning the instrument on the mask, the evaluation of the accuracy and repeatability of the measurements, within a specific measurement campaign is done by observing the values of the maximum deviations for the three colorimetric parameters. With the exception of points 1 and 2, the maximum deviations found were negligible (< 0.5), meaning that the repositioning was performed with good precision. The accuracy and reproducibility of the mask positioning is instead evaluated by observing the trend of the color variation values over time. Also in this case, with the exception of points 1 and 2, the trend proved progressive and constant over time, without marked fluctuations. These measurements therefore appear to be correct and reproducible. For points 1 and 2, on the other hand, higher maximum deviations and a fluctuating trend in the ΔE_{00} value were recorded; it can be assumed that the data were probably affected by errors in repositioning the instrument on the mask and/or errors in repositioning the mask over the measurement area. As regards the chromatic variation of the film-forming material, the results obtained confirm what is visually observable, namely that the applied varnish does not appear to have undergone any appreciable change over the course of five years.

The results obtained are certainly a great incentive to continue this monitoring in the coming years to assess whether the varnish chromatic property is changing. In addition, it is intriguing to understand the role of the underlying paint film in highlighting this change.

6. Conflict of interest declaration

The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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Claudia Gisela Reichold - Trained in Germany, the United States and Italy, she is a Ministry of Culture (MiC) qualified conservator and has worked for 25 years on masterpieces of Museums and Churches in Florence, Italy (Uffizi Galleries, Bargello Museums, Santa Maria Novella and Ognissanti) and for private collections worldwide. After almost 10 years of teaching at University of Dubrovnik, Croatia she collaborates with Italian and American educational institutions and is President of the cultural association ExperienceArt.

Irene Pieralli - Graduated in Science and Materials for Conservation and Restoration of Cultural Heritage from the University of Florence in 2022. Her master thesis work focused on the study of an alternative formulation of Laropal A81 varnish for paintings, free of aromatic solvents and therefore safer for the health of operators and the environment. After graduation she continued her research activity producing various publications, and in 2023 she worked as a conservation scientist for the Florence Museum of Prehistory, supervising the scientific investigations for the façade of the Abbey of San Miniato al Monte in Florence.

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Bestetti R. (2020). *La verniciatura dei manufatti policromi: dalle vernici tradizionali alle resine a basso peso molecolare*, Collana i Talenti. Padova (I): Il Prato.

Chercoles, R., De Tapol, B., Ordoñez, A., & Domedel, L. (2011) Low molecular weight varnishes. Interview to E. René de la Rie, National Gallery of Art, Washington, DC., *Ge-conservación* No. 2, pp. 33-42.

de la Rie, E.R., (1992). *Stability and Function of Coatings Used in Conservation*, National Gallery of Art, Scientific research department, Washington DC 20565, USA.

Johnston-Feller, R. (2001). *Color science in the examination of museum objects: nondestructive procedures*. Getty Publications.

Maines, C.A., & de la Rie, E.R., (2005). Size-exclusion chromatography and differential scanning calorimetry of low molecular weight resins used as varnishes for paintings, *Progress in Organic Coatings* 52, pp. 39-45.

Phenix, A., (1993). Artist's and conservation varnish, an historical overview, in *Varnish theory and practise*, ABPR 50th anniversary Conference, a cura di Padfield S., pp. 12-26. Association of British Picture Restorer.

Pinna, D., Galeotti, M., & Mazzeo, R. (Eds.). (2009). *Scientific examination for the investigation of paintings. A handbook for conservator-restorers*. Firenze (I): Centro Di.

Stoner, J. H., & Rushfield, R. A. (Eds.). (2012). *The conservation of easel paintings*. London: Routledge.

Sharma, G., Wu, W., & Dalal, E. N. (2005). The CIEDE2000 color-difference formula: Implementation notes, supplementary test data, and mathematical observations. *Color Research & Application*, 30(1), 21-30.

Vila, A. & Murray, A. (Eds.). (2022). *Diagnosis: Before, During, After*, Collana Conservation 360°, No. 2, Valencia (E): Universitat Politècnica de València.

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References

Aldrovandi, A., & Picollo, M. (1999). *Metodi di documentazione e indagini non invasive sui dipinti*. Collana i Talenti. Padova (I): Il Prato.

Bacci, M., Casini, A., Cucci, C., Picollo, M., Radicati, B., & Vervat, M. (2003). Non-invasive spectroscopic measurements on the *Il ritratto della figliastra* by Giovanni Fattori: identification of pigments and colourimetric analysis. *Journal of Cultural Heritage*, 4(4), 329-336. doi.org/10.1016/j.culher.2003.09.003.