
Corrosion Detection by Color Change Using Crowdsourced Photographs. Preliminary Results of the MIPAC Project

Blanca Ramírez Barat*

National Centre for Metallurgical Research, Spanish National Research Council (CENIM-CSIC) Madrid, Spain
blanca.ramirez@csic.es

María Teresa Molina

National Centre for Metallurgical Research, Spanish National Research Council (CENIM-CSIC) Madrid, Spain
mt.molina@cenim.csic.es

Emilio Cano

National Centre for Metallurgical Research, Spanish National Research Council (CENIM-CSIC) Madrid, Spain
ecano@cenim.csic.es

*Author for correspondence

Abstract

One of the most obvious signs of metal corrosion is color change. This phenomenon could be used to assess the corrosivity of the indoor environment in museums and collections in other institutions. The MIPAC project is therefore developing a preventive conservation tool for monitoring the impact of the indoor environment on cultural heritage materials, based on the color changes associated with deterioration. The changes are assessed by analyzing photographs taken with cell phones and provided by museum visitors and staff through an app. A color reference chart was designed, in which metal coupons are used as dosimeters. CIELAB color coordinates are extracted from the images and adjusted using the color references with a calibration algorithm. This approach allows the preventive conservation of cultural heritage from both a scientific-technological and a social perspective, since it involves public participation in the conservation of museum collections. However, for this monitoring approach to be valid, the correlations between

color change and corrosion extent need to be determined in order to explore the possibilities of quantifying the extent of corrosion from the calibrated photographs. This paper presents the preliminary results of a validation study, based on tests of a series of copper and silver coupons exposed in museum showcases for 6, 12, and 18 months. Color and corrosion extent measured by gravimetry and galvanostatic reduction showed the good correlation between some of the colorimetric information and the corrosion thickness. Although the uneven distribution of surface corrosion complicates the establishment of a correlation between corrosion and color change, this issue can be tackled by a localized evaluation of the corrosion obtained by electrochemical reduction.

Keywords

preventive conservation, color, monitoring, image analysis, corrosion

Introduction

The degradation of metals and other cultural heritage materials is commonly associated with changes in their visual appearance, especially their color: silver objects darken and tend to blacken upon exposure to sulfur gases; copper turns reddish during the first stages of oxidation and then darkens or assumes a greenish color as corrosion proceeds; iron changes from silvery to reddish with the formation of rust layers; and lead darkens due to the formation of thin lead oxide layers, shifting to whitish as thicker carbonate layers are formed. As corrosion processes are the result of ambient conditions, the color changes of metal references can serve as an indicator of corrosive environments. Thus, the aim of the MIPAC project¹ is to develop a tool that can be used to monitor the impact of the environment on

cultural heritage materials, based on the color changes associated with metal corrosion. The basis of this tool is the relationship between color and corrosion, the ability to monitor color changes through image analysis, and the use of citizen science.

The use of metals and the changes in their appearance as dosimeters to detect aggressive environmental conditions is well established and is the basis of the well-known Oddy test. Colorimetric and spectrophotometric methods have been used elsewhere to determine the color changes in metals as indicators of corrosion (Tétreault et al. 2003, Lafuente et al. 2013), but a quantitative correlation between color change and corrosion extent (quantified as loss of mass or thickness of the base metal, or as the thickness of corrosion layers) has not been established

due to several difficulties (Lafuente 2017). For instance, Ankersmit (2001) reported uneven tarnishing on flat silver samples and an unreliable correlation with the percent color change.

In the MIPAC project, crowdsourced photographs rather than spectrophotometers are used in color evaluation, with the aim of establishing a quantitative correlation between color change and corrosion extent. The feasibility of using cell phone photographs to monitor color changes was demonstrated by Brigham et al. (2018). The use of citizen science as a data collection method has two major advantages: first, it does not require investments of additional resources by the museum, and second, it actively involves the public in museum practices and the conservation of museum objects.

In the MIPAC's approach, copper and silver strips acting as dosimeters are mounted as a color reference chart for use in image calibration, as shown in Figure 1 (Ramírez Barat et al. 2021). The "MIPAC panels" are displayed in the locations to be monitored.



Figure 1. MIPAC panel for the monitoring of color changes of metal coupons. The color chart was printed using UV resistant inks on acid-free paper covered with propylene

For image collection, a dedicated app² was created that allows for better control of the cell phone camera and the automatic uploading of photographs to the image-processing servers. The integration of a gamification scheme in the app promotes user engagement.

To extract the color information from the photographs, an image calibration system was designed and subsequently validated in collaboration with the Visual Telecommunications Applications Research Group (GATV) from the Technical University of Madrid (UPM) (Barbero-Álvarez et al. 2020, Barbero-Álvarez et al. 2021a). MIPAC panels are photographed by visitors and the images are then processed and calibrated by applying linear and spatial calibration algorithms to obtain corrected $L^*a^*b^*$ coor-

dinates of the metal dosimeters, which are then related to the extent of corrosion. The robustness of the calibration method and its ability to adjust for the color differences in cell phone images from different cell phones have been demonstrated (Barbero-Álvarez et al. 2021b), and tests with real metal samples conducted. The results have thus far shown that color changes are detected with a high degree of confidence, as shown by comparisons with direct colorimetric measurements made using a spectrophotometer (Table 1) (Ramírez Barat et al. 2021). This allows at least to detect significant changes in the metal dosimeters that act as indicators of the presence of harmful emissions in a museum showcase or location.

Table 1. Measured and calculated $L^*a^*b^*$ coordinates for a silver coupon (from Ramírez Barat et al. 2021)

12A_Ag	Measured	Calculated
L^* (10°/D65)	72.44	68.45
a^* (10°/D65)	5.00	4.64
b^* (10°/D65)	26.82	26.55

An important step to improve the precision and reliability of the method is to establish a quantitative relationship between color changes and corrosion extent. Ideally, a calibration curve between color coordinates and corrosion thickness would allow to measure the corrosion of metals and classify the corrosivity of a museum environment, using the MIPAC panels as dosimeters. Accordingly, we examined the correlation between corrosion extent and color change in copper and silver coupons exposed to real museum environments for up to 18 months at the National Museum of Science and Technology (MUNCYT) and at the museum of the Chemistry Faculty of the Complutense University, both located in Madrid.

Experimental

To analyze the relationship between color and corrosion extent, 1×5 cm copper and silver coupons were cut, drilled, sanded with P1200 grit, and mounted on a MIPAC color reference panel (Figure 1). The panels were placed inside four different museum showcases (labeled S1 to S4), two in each of the two aforementioned museums (Figure 2).

Additional sets consisting of 12 coupons of each metal were hung on plastic racks, according to ISO 11844-2 standard (International Organization for Standardization 2020), and exposed in the same locations. From this racks,



Figure 2. The MIPAC panel monitoring inside a showcase at the Faculty of Chemistry of Complutense University, together with a set of copper and silver coupons on plastic racks (left side)

four coupons of each metal were extracted after 6, 12, and 18 months to measure the color change and quantify the corrosion extent by gravimetry and galvanostatic reduction, following the procedures established in ISO 11844-2 standard. For the electrochemical measurements, a GAMRY Interface 1000 potentiostat was used, together with a three-electrode cell with a Ag/AgCl reference electrode, a graphite counter electrode, and deaerated KCl 0.1 M as the electrolyte, with constant N_2 bubbling. Reduction was done in delimited areas of the coupons using a vinyl tape mask. The four coupons at each time point were subjected to gravimetric evaluation, while reduction was performed on six areas of one coupon for each showcase and exposure time.

Color was measured in the $L^*a^*b^*$ color space using a Konica Minolta CM-700d spectrophotometer with an \varnothing 6 mm mask, D65 as the illuminant, and an observer angle of 10° . Six color measurements were performed, in the lower, central, and upper parts of each side of the coupon, to obtain an average value per coupon. Six measurements were also made in each reduced area.

Results and discussion

The metal coupons showed mild corrosion after exposure in the museum cases, with differences observed depending on the location. Visually, the silver coupons had a yellowish hue that was clearly darker at the edges and in the lower area of the coupon. By contrast, the copper coupons underwent only slight changes, not perceivable at first sight, as they remain within their natural reddish color range.

Corrosion was measured by gravimetry as mass gain, with the values then transformed to the thickness of the corrosion layer by assuming that the composition of the corrosion layer was silver sulfide (Ag_2S) for the silver coupons and cuprite (Cu_2O) for the copper coupons. The plot of the corrosion layer thickness versus the colorimetric coordinates $L^*a^*b^*$ is shown in Figure 3. The most evident feature of both metals is a reduction in lightness as the thickness of the corrosion layer increases. For the silver coupons, changes in the a^* axis are minimum, but a tendency toward yellowing is evident by the increase in b^* . The chromaticity changes in the copper coupons are smaller, as the hues are slightly warmer, with a minimum increase of a^* and a moderate increase of b^* .

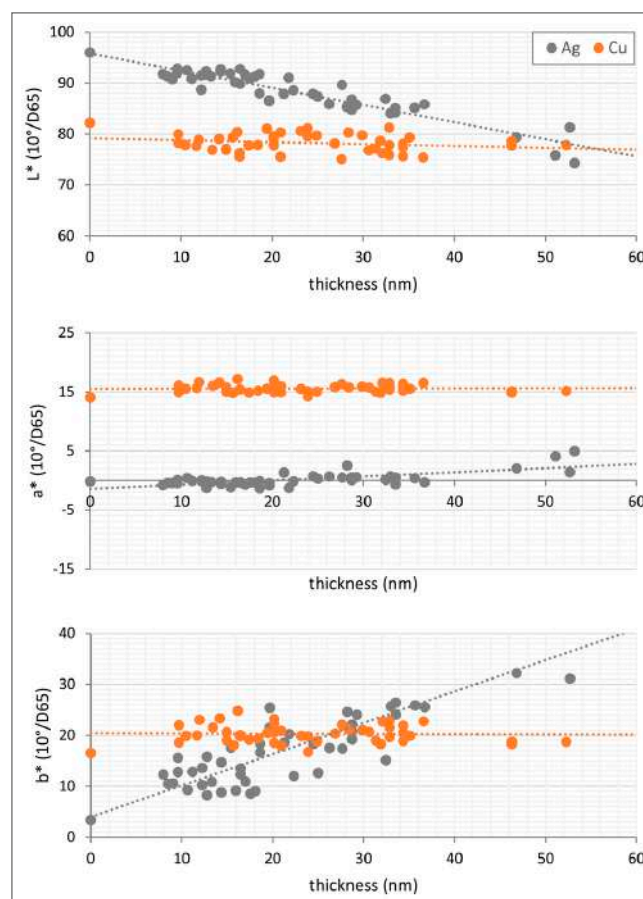


Figure 3. Correlation between corrosion thickness (measured using the gravimetric method) and the $L^*a^*b^*$ coordinates for silver and copper

As previously indicated, the distribution of corrosion is visibly irregular, particularly for silver. In addition to the concentration of the corrosion at the borders of the coupons, a comparison of the average values of $L^*a^*b^*$ for the lower, center, and upper areas of different sets of coupons (Table 2) showed that the lower areas are generally darker and yellower (lower L^* , higher b^*).

The fact that the gravimetric determination of the mass or thickness of the corrosion products provides an average value for the whole surface detracts from the accuracy of the correlation between the color and concentration of the corrosion products. Therefore, the extent of corrosion was also assessed by galvanostatic reduction, using localized areas of the silver coupons. Up to six circular areas of several silver coupons were isolated with tape and galvanostatically reduced. The corrosion layer thickness was calculated using Faraday's law, following the ISO 11844-2 standard (ISO 2020). Color was also measured in those areas. The results and a comparison with the gravimetric data are presented in Figure 4. The most evident difference is that the electrochemical techniques indicate a more pronounced color variation with the increasing thickness of the corrosion layer. The reduction of a defined area, coincident with the area of measured color, increases the sensitivity of the method. In the gravimetric method, which provides average values for the whole coupon, the higher concentration of corrosion products at the edges is reflected in the weight gain but not in the color variation. These results show that a localized measurement of color together with electrochemical reduction solves the unreliability of color measurements in flat silver samples reported by Ankersmit (2001).

While the data thus far suggested that the variation of $L^*a^*b^*$ coordinates is more or less linear, the number of items in the data set at this stage of the project is too small to draw final conclusions.

To test the applicability of the MIPAC system, the color coordinates extracted from a photograph of a real metal coupon from the MIPAC panel (Table 1) obtained in a previous work (Ramírez Barat et al. 2021) are included in Figure 4, labeled as 12A_Ag. The corrosion layer thickness of this coupon (part of another project) was also calculated by gravimetry and galvanostatic reduction of the whole surface.

Although this is only one data point, and its value fell at the extreme of the calibration range for corrosion layer thickness, for which only a small number of data are available, it can be considered a reasonable result. With the use of gravimetric values, the lightness value of 12A_Ag was much lower than the general trend (even compared to the spectrophotometric value of 72.44): a^* was slightly higher while b^* fit well. With the galvanostatic results, fitting was satisfactory for the L^* and a^* coordinates. For the b^* coordinate, however, the value

Table 2. $L^*a^*b^*$ coordinates in the lower, central, and upper areas of exposed silver coupons. The average values for each set of samples at four different locations (S1–S4) after 6, 12, and 18 months of exposure are shown

$L^* (10^\circ/D65)$						
sample/ exposure time	bottom	σ	center	σ	up	σ
S1 / 6 m	87.01	1.27	87.08	1.17	87.48	1.22
S2 / 6 m	91.01	0.88	91.21	0.86	91.26	0.91
S3 / 6 m	91.37	0.87	92.04	0.53	91.81	0.54
S4 / 6 m	88.31	2.46	88.47	2.65	86.25	3.53
S1 / 12 m	84.44	2.44	85.45	2.85	85.48	2.34
S2 / 12 m	88.99	1.39	89.85	1.38	89.57	1.59
S3 / 12 m	91.49	0.54	90.91	0.50	91.77	0.14
S4 / 12 m	92.58	1.18	92.71	1.07	92.42	1.74
S1 / 18 m	76.19	5.20	78.81	4.08	78.07	4.33
S2 / 18 m	82.38	2.59	85.94	1.56	86.91	1.12
S3 / 18 m	91.21	0.67	91.27	0.46	92.39	0.48
S4 / 18 m	84.74	1.28	86.93	2.26	86.30	1.44

$a^* (10^\circ/D65)$						
sample/ exposure time	bottom	σ	center	σ	up	σ
S1 / 6 m	0.31	0.37	0.25	0.32	0.14	0.32
S2 / 6 m	-0.47	0.14	-0.41	0.15	-0.35	0.12
S3 / 6 m	-1.38	0.29	-1.19	0.27	-1.23	0.16
S4 / 6 m	0.53	1.19	1.09	0.98	2.11	2.09
S1 / 12 m	0.57	0.55	0.41	0.74	0.20	0.62
S2 / 12 m	-0.25	0.16	-0.20	0.15	-0.18	0.21
S3 / 12 m	0.57	0.11	0.41	0.07	0.20	0.13
S4 / 12 m	-0.25	0.33	-0.20	0.07	-0.18	0.51
S1 / 18 m	4.08	3.07	2.50	1.78	2.80	2.25
S2 / 18 m	1.19	1.07	0.36	0.58	0.10	0.54
S3 / 18 m	0.04	0.12	-0.10	0.04	0.22	0.52
S4 / 18 m	-0.48	0.43	-0.52	0.68	-0.66	0.31

$b^* (10^\circ/D65)$						
sample/ exposure time	bottom	σ	center	σ	up	σ
S1 / 6 m	14.41	2.86	14.28	2.56	14.38	2.28
S2 / 6 m	9.47	1.22	8.94	1.02	8.41	0.61
S3 / 6 m	17.90	3.10	16.37	2.50	17.90	2.57
S4 / 6 m	18.29	5.21	18.50	5.24	22.47	7.69
S1 / 12 m	22.09	3.54	21.16	5.25	22.68	4.72
S2 / 12 m	14.96	4.17	12.46	2.56	12.79	1.90
S3 / 12 m	10.89	0.48	10.69	0.42	11.76	1.21
S4 / 12 m	15.06	3.37	13.13	3.26	14.38	4.99
S1 / 18 m	39.60	10.84	36.12	7.86	36.43	9.02
S2 / 18 m	30.47	5.06	21.86	1.87	20.31	1.41
S3 / 18 m	11.23	1.89	10.52	2.19	8.81	1.10
S4 / 18 m	27.66	4.25	23.97	5.91	22.68	3.76

was expected to be yellowish. As the calculated coordinate was close to the true measured one, the apparent mismatch cannot be attributed to the calibration method. A possible explanation is the evolution of colors in silver tarnishing, particularly along the yellow-blue axis. Tarnish layers initially have a yellowish color, but they can later acquire bluish tones and thick layers become black. Consequently, the trend in the evolution of the b^* coordinate may differ depending on the thickness intervals. This behavior was suggested in previous works in which colorimetric measurements were used to quantify silver tarnishing, based on comparisons of reflectance (in %) with an ideal reflecting diffuser (Ankersmit 2001, Ankersmit et al. 2013).

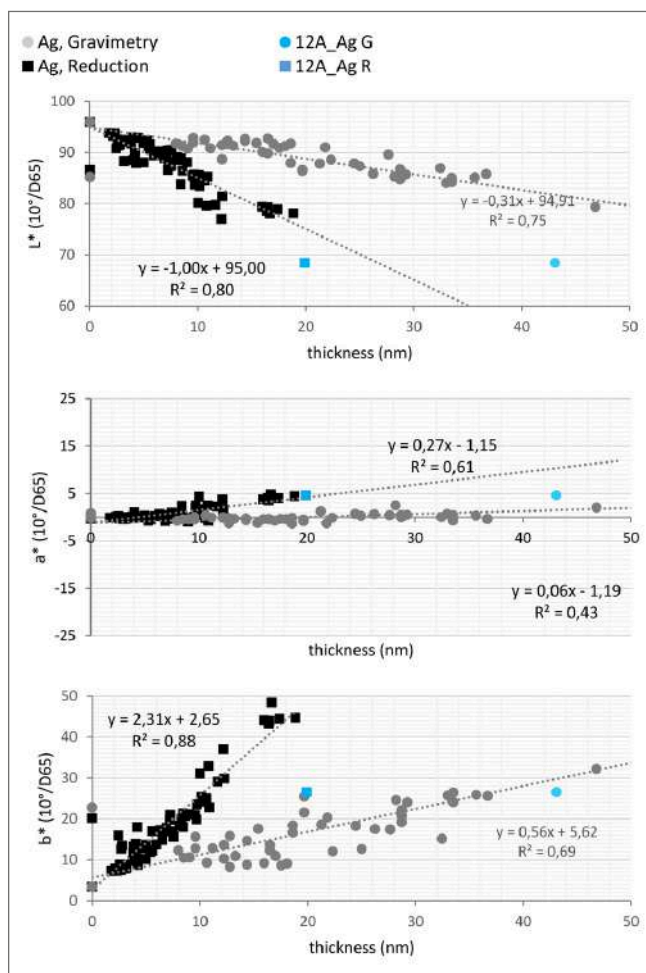


Figure 4. Correlation between corrosion thickness and the $L^*a^*b^*$ coordinates for silver. Comparison of gravimetric and galvanostatic reduction results. The $L^*a^*b^*$ coordinates of sample 12A_Ag extracted from an image of a MIPAC panel and then calibrated are also plotted vs. corrosion thickness, calculated by gravimetry (12A_Ag G) and following galvanostatic reduction (12A_Ag R)

Conclusion

The results presented in this work, on the tarnishing of silver and copper coupons exposed to real museum

environments for up to 18 months, showed that for both metals the amount of corrosion correlated well with the color changes. While the main change was in lightness, a good correlation with the chromaticity changes was also observed.

The problem of the dispersion of the data due to uneven tarnishing can be largely solved by using localized reductions and color measurements in small areas of the coupons.

Further studies, at longer exposure times and in different museum environments, are necessary to understand the correlations for thicker corrosion layers. This work is currently in progress, with more complete results expected in the coming months.

The good correlation between corrosion and color change as well as the good results obtained in the calibration of photographs, as reported in previous work by the authors, are very promising for the proposed MIPAC system. Its full implementation will provide a flexible, scalable, and low-cost solution to the collection of conservation data in addition to encouraging society's commitment to its heritage.

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Notes

¹ Monitorización por procesado de imagen y ciencia ciudadana para la conservación de materiales del patri-

monio cultural (MIPAC-CM) (Monitoring by image processing and citizen science for the conservation of cultural heritage materials) is a research project funded by Comunidad de Madrid and the European Union. www.mipac-cm.es/

² <https://play.google.com/store/apps/details?id=com.norrispalmer.mipac>

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Authors

Blanca Ramírez Barat obtained a BA in fine arts (conservation), after which she focused on heritage science, graduating with a degree in chemistry (UCM University) and obtaining a PhD in materials science and engineering (UC3M University). Since 2013 she has worked at the CENIM-CSIC on the application of electrochemistry to the conservation and diagnosis of metallic heritage. She has participated in several national and European research projects, as well as different initiatives related to heritage science, including the TechnoHeritage network, the National Conservation Research Plan, the CSIC Interdisciplinary Platform Open Heritage: Research and Society, and the Spanish Node of the European Research Infrastructure in Heritage Science (ERIHS.es).

María Teresa Molina has a BA in conservation and restoration of cultural heritage and a MSc in science and technology of architectural heritage from the University of Granada. She has worked as an R+D+I technician

in the Department of Mineralogy and Petrology of the University of Granada in topics such as the deterioration of heritage materials by exposure to environmental and atmospheric agents. Since 2019, she has been working on her PhD thesis in materials science and engineering at the CENIM-CSIC. Her work is focused on the conservation of metals in scientific-technical heritage.

Emilio Cano is senior scientist at the CENIM-CSIC in Madrid. He is head of the “Atmospheric Corrosion and Cultural Heritage Conservation” (CAPAC) research group, dedicated to studies of corrosion, the protection of metallic heritage, atmospheric corrosion, and electrochemical techniques. He is the author of more than 90 articles and 100 contributions to conferences. He is a Fellow of the IIC and was assistant coordinator of the ICOM-CC Metals Working Group (2012–2020). He is a member of the coordination team of the CSIC Interdisciplinary Platform “Open Heritage: Research and Society” and National Coordinator of the Spanish Node of the European Research Infrastructure for Heritage Science (E-RIHS).