

Vectorial versus functional statistical approaches to evaluate colour variations of tempera paints exposed to real environment

Teresa Rivas¹, J. Santiago Pozo-Antonio², Diana Barral³, Javier Martínez⁴, Carolina Cardell⁵

¹ *Dept. de Enxeñaría dos Recursos Naturais e Medio Ambiente, Universidade de Vigo, 36310, Spain, trivas@uvigo.es*

² *Dept. to de Enxeñaría dos Recursos Naturais e Medio Ambiente, Universidade de Vigo, 36310, Spain, ipozo@uvigo.es*

³ *Dept. de Enxeñaría dos Recursos Naturais e Medio Ambiente, Universidade de Vigo, 36310, Spain, dianabarral@uvigo.es*

⁴ *Centro Universitario de la Defensa, Escuela Naval Militar, Plaza de España, 36920, Marín, Spain, javier.martinez@tud.uvigo.es*

⁵ *Dept. of Mineralogy and Petrology, University of Granada, 18071, Spain, cardell@ugr.es*

Abstract – The colour changes of tempera paints exposed to the ambient depends on the composition of the paint (pigment, binder and the interaction between them) and the components of the atmosphere. In this paper several statistical techniques based on vector and functional approaches are presented in order to accurately establish the trends of colour changes of paint mock ups composed of different pigments and binders and exposed to a real ambient. A functional approach of the statistical techniques applied are revealed much more useful than a vectorial (classic) approach in order to extract information about the colour variations during the exposure.

I. INTRODUCTION

Tempera painting is a technique where inorganic pigments are mixed with protein binding media such as rabbit glue, casein or egg yolk [1]. When these kind of paintings are exposed to the ambient, they can suffer different alteration processes that depend on the nature of the binder and the pigment and on the interaction between both components. Also, these alteration processes will be different attending to the environment: marine influence or/and presence of pollutants from traffic and industrial activities.

So, depending on the binder, the painting surface has different roughness and colorimetric characteristics and therefore its response to ageing process will be different [2]. On the other hand, inorganic pigments can suffer chemical alterations through the interaction with moisture and air components (O₂, NO_x, CO₂, SO₂, SO₃ and H₂S), resulting in changes in the colours of the paintings [3]. The exposure to O₂, atmospheric sulphur-containing

compounds or CO₂ can lead to chemical alterations and mineralogical transformations of the pigment compounds, such as minium to plattnerite (PbO₂) [4], lead-based pigments to black galena (PbS) [5] or azurite to basic copper carbonates or copper sulphates chlorides [6].

Also, the interaction between metallic pigments (Zn, Mn or Cu based pigments) and the binder can result in the production of metal soaps in the surface of the painting modifying the appearance of the paintings [7].

One of the most immediate visible effect derived from the impact of the environment in an artistic painting is a change in its colour. So, the analysis of the paints in the visible and infrared spectrum would allow to monitor the compositional changes and therefore to identify the deterioration processes that would subsequently investigated with other analytical techniques. Thus, colorimetric methods, applied in order to monitor the changes of paint mock-ups subjected to accelerated aging tests and to natural exposure assays, are a potential tool in preventive conservation. Nevertheless, these methods, commonly applied in the monitoring of the deterioration of materials such as rocks, plastics and wood [8-9], are poorly developed in the case of pictorial cultural heritage.

In this study the results of the evaluation of colour changes suffered in a set of tempera paint mock-ups exposed during 13 months to a natural atmosphere characterized by an important marine and industrial influence are presented. Paint mock-ups were manufactured using 7 different inorganic pigments with variable grain sizes and mixed with two types of binder.

The main contribution of the present study is the exploration of the suitability of several statistical approaches, which go beyond a purely descriptive statistics, in order to identify trends and similarities in

colour changes of the paints during the exposition.

In the studies on the evaluation of colour variation of materials subjected to natural or artificial environments, the impact on the colour is performed quantitatively by calculating the colorimetric differences in the colour spaces most used (CIEL*a*b* and CIEL*C*h*) [10,11]. But, this type of descriptive approach is not satisfactory to deal with, for example, the study of variation in colour when multiple variables or factors of variation are considered [12] or in time series studies. Thus, in the trial performed in this study, the variability in composition of the paintings (related to pigment and/or binder) and texture (grain size of the pigment) implies the existence of a large number of variables or factors of variation which requires the application of a statistical methodology that also can be adapted to the analysis of colour measures depending on time (functional approach).

II. MATERIALS AND METHODS

A. *Tempera mock-ups and exposition conditions*

36 samples (tempera paint mock-ups) composed of 7 pigments with different grain sizes mixed with two different binding media (egg yolk or rabbit glue binder) were prepared according to Old Master recipes to obtain

standards similar to those used by medieval artists [13]. Pigments from Kremer (Table 1) were used: white pigments (chalk, gypsum and white lead); red pigments (hematite and cinnabar) and blue pigments (azurite and lapis lazuli). Different grain sizes of the pigments were used (Table 1); laser diffraction particle size analysis was applied to obtain the particle size distribution. These pigments were mixed with two different binders, egg yolk and rabbit glue, in a ratio pigment: binder needed to obtain a workable tempera paint.

After the preparation of the tempera and once dried, mineralogical composition was obtained according to X-ray diffraction (Table 1).

The paint mock-ups were placed in an open balcony faced to the Atlantic Ocean in Vigo (Galicia, NW Spain) during 13 months.

The ambient of exposure in this place is characterized by a high influence of sea spray and atmospheric pollutants derived from traffic and industrial activity [14]; the main inorganic contaminants in this site are chloride (from marine origin), SO₂ (derived both from anthropogenic sources and marine aerosol) and, in a lesser extent, nitrates (derived from farming).

Table 1: Basic information of the paint mock-ups: colour, mineralogical composition and maximum particle (μm) of the pigments used to prepare de samples with egg yolk and with rabbit glue. C: calcite; P: portlandite; D: dolomite; A: anhydrite; B: basanite; G: gypsum; HC: hydrocerussite; CE: Cerussite; m H: hematite; Q: quartz; GO: goethite; CI: cinnabar; Sil: other silicates; AZ: azurite; M. malachite; L. lapislazuli.

Sample	Colour	Mineralogical composition	Maximum particle size
1 Chalk, extra fine	white	C, D, Q	25
2 Chalk, coarse	white	C, P	60
3 Chalk, extra coarse	white	C, P	120
4 Gypsum, medium	white	G, B	7
5 Gypsum, fine	white	G, A, B	16
6 Gypsum, extra fine	white	G, A	9
7 White lead	white	CE, HC	3
8 Hematite, extra fine	red	H, D, Q, GO	0,6
9 Cinnabar, extra fine	red	CI	12
10 Cinnabar, medium	red	CI, Q	48
11 Cinnabar, coarse	red	CI, Q	75
12 Cinnabar, extra very fine	red	CI, Q, Sil	8
13 Azurite, extra coarse	blue	AZ, Q, M	90
14 Azurite, coarse	blue	AZ, Q, M	70
15 Azurite, medium	blue	AZ, Q, M	45
16 Azurite, extra fine	blue	AZ, Q, M	25
17 Azurite, extra very fine	blue	AZ, Q	22
18 Lapis Lazuli	blue	L, C, D	47

B. Analytical techniques

During 13 months, the colour of each paint mock-up was characterized each 50 days, by means CIEL*a*b* and CIEL*C*h* colour spaces and using a Minolta CM-700d spectrophotometer. L*, a*, b*, C*_{ab} and h*_{ab} parameters were measured. 18 random measurements for each sample were obtained. The measurements were made in the Specular Component Included (SCI) mode, for a spot diameter of 3mm, using D65 as illuminant and an observer angle of 10°.

C. Statistical methods

The classical vector analysis was performed using a box and whiskers plots whose main characteristics are: 1) the boundaries of each box correspond to the first and third quartile of the sample; 2) the centre line corresponds to the median; 3) the ends of the whiskers (dotted lines) identify the extreme values, 1.5 times the interquartile range from the ends of the box; 4) outliers, i.e. those elements of the sample that fall outside of these extremes, are identified by a star. This type of analysis is very useful to analyse two types of features:

- Trend: The position of the box as a whole along the time instants analysed, allows to determine whether the sample shows a trend regarding the considered parameter.
- Homogeneity: Analysing the width of the box at each time instant, it is possible to determine the evolution of the homogeneity of the behaviour within the sample over time.

Functional analysis allows to treat a set of data as continuous measurements, transforming an initial vector problem in a functional problem. This allows to analyse the trend and periodicity of measurements without considering possible measurements errors of discrete character, which may be considered insignificant due to their origin and occurrence. Functional approach has also an added advantage regarding the vast majority of criteria outlier detection, so it does not require a normally distributed sample data or a transformation needed for that purpose.

More in detail, given a set of observations $x(t_j)$ contained in a set of n_p points where t_j represents each instant of time and n_p the number of observations ($j = 1, 2, \dots, n_p$), all observations can be considered as discrete observations of a function $x(t)$ in F , where F is a functional space. For convenience, the following expansion is considered for recording function [14]:

$$x(t) = \sum_{k=1}^{n_b} c_k \phi_k(t) \quad (1)$$

which c_k represents the coefficients of the function $x(t)$ with respect to the set of selected basic functions.

The first phase of functional analysis is the process of smoothing which allows to solve the following problem

regularization [15]:

$$\min_{x \in F} \sum_{j=1}^{n_p} \{z_j - x(t_j)\}^2 + \lambda \Gamma(x) \quad (2)$$

Once the data is transformed into functional data, they are already prepared for the jump to the second phase, in which they can be analysed to detect outliers using the concept of functional depth. This concept provides a sorting criteria for a set of points contained in a Euclidean space, from its center to the periphery. According to this criterion, the nearest to a point the center is, the greater its depth is. In multivariate analysis, the depth is usually used as a measure of the centrality of a point from a point cloud [16]. Considering the functional problem [17], the depth represents the centrality of certain curve contained in a set of curves. Therefore, based on the functional depth, those functions with lower depths are identified as outliers.

After the calculation of the functional depths, a third phase is performed, which consists on the analysis of the outliers of the sample. For this, the cutoff value (C) is estimated from bootstrapping approximation method. Cutoff value was selected so that the percentage of observations misidentified as outliers was about 1% [18].

III. RESULTS AND MAIN CONCLUSIONS

In both type of analyses, three variables were analysed: ΔL^* , ΔC^*_{ab} and ΔE^*_{ab} . Differences between the values of these variables obtained for rabbit glue tempera and the values for the same variables obtained for the egg tempera were used as data sample. So, the proposed analyses, both vector and functional, focus on evaluating the differences in behaviour during the exposition among each family colour tempera depending on the nature of the binder (egg and rabbit).

Both approaches, vector and functional, give similar information concerning the trend of L^* and C^*_{ab} (ΔL^* and ΔC^*_{ab}) and total colour change (ΔE^*_{ab}) of each group of tempera (made with egg or made with glue rabbit) and also concerning the homogeneity in the behaviour of samples of each family colour tempera during exposure:

- 1) Regarding white paints, it is observed that, in the first instants, ΔC^*_{ab} is much more intense in egg tempera paints than in rabbit glue tempera paints (Figure 1a); afterwards, the difference in the behaviour between the two types regarding chroma tends to diminish, showing the two groups of paints a similar trend during time. Also, an increase on the dispersion within the white tempera family as exposure time elapses is observed, especially regarding ΔL^* and ΔE^*_{ab} (Figure 1b). This increased dispersion could be due to differences in mineralogical composition among the white tempera paints samples, which would determine a different deterioration during the exposition and consequently a different colour change

trend.

2) In the red samples, the results also clearly show a different behaviour between egg paints and rabbit glue paints regarding the three colour parameters but specially in ΔC_{ab}^* parameter (Figure 1c): the tempera paints made with egg undergo a larger change than the paints made with rabbit glue. Also observed is an increased dispersion within this red tempera sample as the time exposure progresses; since almost all the red tempera paints are made with the same pigment (cinnabar), the increased dispersion could be due to a different response of the paints to the ambient exposition due to the different grain size of the pigment.

3) In the blue coloured paints, it is also observed that egg made tempera show a more intense variation in ΔC_{ab}^* parameter than rabbit glue paints (Figure 1d).

Nevertheless, this happens in the first instants; as the exposure time progresses, the differences between the two groups of samples are reduced.

Although both analytical approaches, vectorial and functional, give identical information on the trend and the homogeneity in the behaviour during time, functional approach has, however, an advantage over the vectorial approach because it allows to discriminate atypical behaviours within each colour family of tempera. Thus, the results of the analysis of ΔE_{ab}^* variation of blue paints, vectorial approach identifies two atypical behaviour: the sample 17 (made with the extra very fine grained Azurite) in four different instants during the exposition and sample 15 (made with the medium grained Azurite) in two instants (Figure 2a).

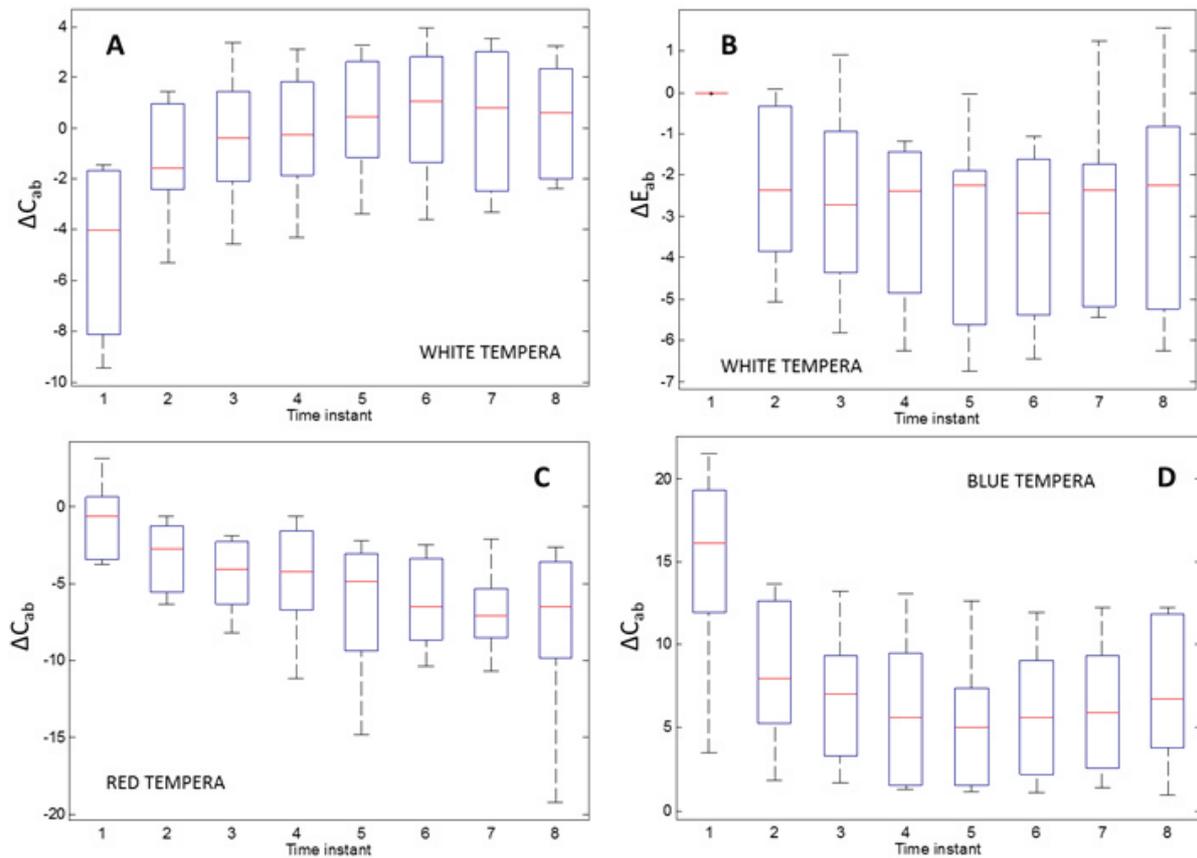


Figure 1: Box plots of variable difference between rabbit glue tempera data and egg tempera data. A) Variable= ΔC_{ab}^* for white tempera; B) Variable= ΔE_{ab}^* for white tempera; C) Variable= ΔC_{ab}^* for red tempera; D) Variable= ΔC_{ab}^* for blue tempera.

However, functional analysis indicates that only the sample 17 shows a statistically significant atypical behaviour: in Figure 2a, it can be seen that the curve of this sample is placed far above the curves of the other samples of the group. Functional analysis also identifies an unusual behaviour that goes unnoticed for the vectorial approach: in the analysis of the variation of ΔL^* variation on the red tempera group, a statistically significant atypical behaviour is detected in sample 9 (cinnabar, extra fine) (Figure 2c).

In conclusion, the application of a functional approach seems to be most suitable to be applied in this case study.

This approach allows to detect the differences among the set of samples concerning the trend of the colour variation during time and also the degree of homogeneity of that change within each group; but, it also allows to detect statistically significant outliers. Further analyses based on this functional approach would allow to more rigorously identify the intrinsic factors related to the paints (grain size and mineralogical composition) causing the variation in colour parameters during the ambient exposition but even to predict the behaviour of the different tempera.

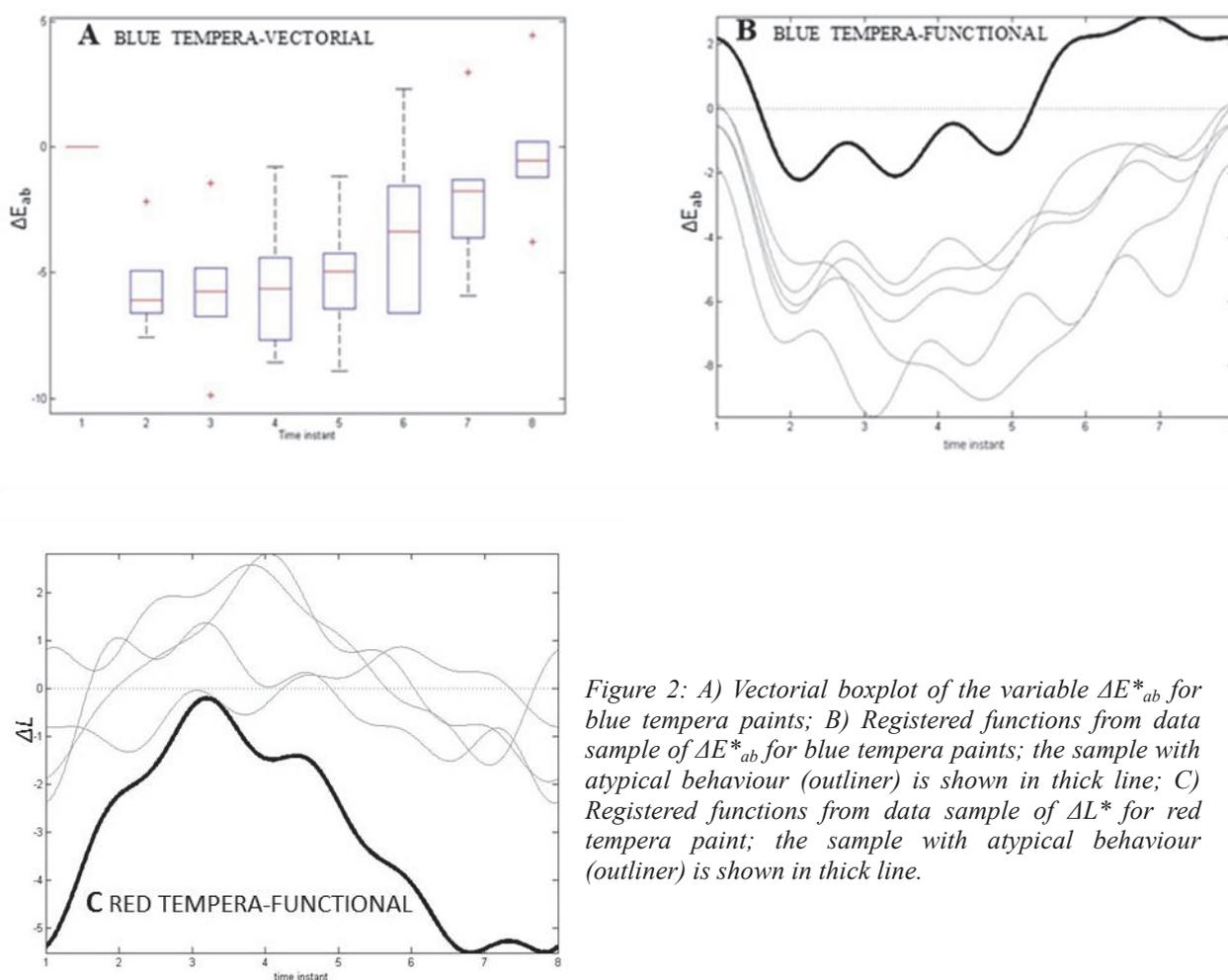


Figure 2: A) Vectorial boxplot of the variable ΔE_{ab}^* for blue tempera paints; B) Registered functions from data sample of ΔE_{ab}^* for blue tempera paints; the sample with atypical behaviour (outliner) is shown in thick line; C) Registered functions from data sample of ΔL^* for red tempera paint; the sample with atypical behaviour (outliner) is shown in thick line.

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