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Effect of the application technique on the colorimetric coordinates for a ceramic enamel

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Abstract. In ceramic tiles production processes for ornamental purposes, the industry uses enamel as raw materials that support the pigments that give coloration and tonal constancy in a glassy matrix. These parameters are of great interest in the acceptance of the final product by the consumer. Due to the increasing number of complaints related to variations in tone in ceramic enamel of the tiles produced by a ceramic company in northeastern Colombia, this work studied the enamel approval methodology's effect on the final tone of the ceramic pieces. A ceramic enamel was prepared and applied by the enameling pad technique on tiles manufactured by dry pressing. By applying the spectrophotocolorimetric technique, the colorimetric parameters were determined. The Tukey test's statistical results did not show statistical significance in the tile samples' tonal variation.

1. Introduction

In the industry for producing ceramic tiles for aesthetic or decorative applications, different types of engobes and colored enamel are used, which give the substrate characteristics of gloss, texture, and color [1]. The quality control of ceramic products is based on the tone, which is the attribute of a visual sensation according to which a surface appears to be similar to one of the perceived colors, red, yellow, green, or blue or a combination of two of them. It is a variable that depends on many factors: enamel composition, pigment concentration, the reaction of the ink with the support, texture, ceramic defects, physical response of the vitreous matrix with light, among others [2]. The sensation of color depends on factors such as the object, the observer, and illuminant, the geometry, the area, surface, brightness, temperature, among others [3]. Colorimetry is the science that studies the measurement of color by developing methods for its quantification [4-6]. These methods are specifically based on the geometry and spectral distributions of three elements: the light source, the reflectivity of the sample, and the visual sensitivity of observers [7-10]. This science transforms sensory perception into numbers, measuring, comparing, and reproducing the different colors [11-13].

The Commission Internationale d'Eclairage $L^*a^*b^*$ (CIELAB) space, it has been used space as quality control factors depending on the industry and activities in which it is used, such as the textile [14], paints, ceramic [15], and in all sectors [16]. Within the CIELAB space, three of the registered coordinates are L^* , a^* , and b^* . The L^* coordinate represents the luminosity, while the a^* and b^* coordinates express the color wheel. In this way we can calculate the variations $\Delta L^* = L^*_1 - L^*_0$, $\Delta a^* = a^*_1 - a^*_0$ y $\Delta b^* = b^*_1 - b^*_0$. These values are used to find the global change in color between two tints (ΔE^*_{ab}). The variation ΔE^*_{ab} is calculated as the Euclidean distance between the points resulting from



its representation in space, so $\Delta E^*_{ab} = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$. Low values of ΔE^*_{ab} correspond to small color differences [17]. On the other hand, chromaticity (C^*) indicates how pure, intense, or vivid color is on a scale from 1 to 100, where the latter value expresses the highest purity [18]. Due to the variability of raw materials, the formulation and color adjustments of enamel in the ceramic industry are usually an empirical procedure, making it difficult to control [19]. On average, the Colombian ceramic industry receives about 4000 requests, complaints or claims, associated with the good offered, of which more than 1000 are accepted. That is, approximately 25% of them. The leading causes of claims regarding the difference in tones [20].

In the development of this research, it was proposed to evaluate the influence of the technique of applying a ceramic enamel on the color coordinates L^* , a^* , b^* [21-23], and Tukey test because it was identified that they are parameters little controlled by the operators and that result in quality control of the final product.

2. Materials and methods

This section describes the characteristics of the enamel and its application on the ceramic substrate.

2.1. Enamel elaboration

A ceramic enamel colored with reference pigments PG56049 and PG53025 from the Colorobbia® was used in the development of the tests. The viscosity, retention, and density values of the enamel were kept fixed. For the preparation, to 2472 kg of transparent type were added 1 kg of industrial salt, 850 liters of water, 2200 kg of Torrecid's® MGC-00159 glossy enamel, 3.5 kg of P2-10 gelycel as a bactericide, 5 kg of sodium tripolyphosphate, 0.5 kg of 100052 Texilan 1560, 4 kg of 50 mm alumina balls, 220 kg of F-6468 frit, 44 kg of Kaolin MGH-00118 from Torrecid Mex® to an industrial ball mill. It is carried out grinding for nine hours. After grinding, the company's enamel acceptance conditions: density in the range from 1795 to 1805 g/l, retained between 10 and 10.5 in 250 μ m mesh. Rheology in 273 cP, 8.5 kg of PG56049 pigment, and 0.8 kg of Colorobbia® pigment PG53025 are additionally added to the BP2 colored enamel with a brown appearance.

2.2. Enamel application

The enameling pad is an instrument made of AISI 304 stainless steel measuring (149 x 60 x 36) mm with fixed 0.3 mm openings to apply ceramic enamels. The applications were made in the industrial process on (450 x 450 x 8) mm tiles manufactured by dry pressing from the production line. When applying the enamel, an operator places a piece of paper between the ceramic substrate to prevent it from adhering to the substrate. Afterward, 100g of enamel is deposited, and it slides at speed. Constant on the ceramic substrate, leaving two stripes that allow the applications to be compared.

2.3. Characterization equipment

Fieldwork was carried out with three operators (treatments) and three replications, on three consecutive days. The test consisted of applying colored ceramic enamel BP2 on ceramic substrates glued at an average temperature of 45 °C. For the determination of the coordinates L^* , a^* , b^* , the surface of the sample was cleaned with industrial alcohol. A PCE-CSM 7 colorimeter equipment with illuminant D65 was used, which was duly calibrated to a tolerance of 0.001. The one-way analyzes of variance used were obtained with the data analysis tools of the R software.

3. Results and discussion

The values of the L^* , a^* , and b^* coordinate obtained in the tests carried out with the operators for the three test days are recorded in Table 1. In Table 1, the L^* coordinate represents the luminosity, taking values from 0 (black) to 100 (white), while the a^* and b^* coordinates express the color wheel, taking values from $+a^*$ (red) to $-a^*$ (green) and from $+b^*$ (yellow) to $-b^*$ (blue). The statistical significance level was used to analyze the information collected in this research $\alpha = 0.05$ and the F test statistic. The results of the analysis of variance for the variables L^* , a^* , and b^* are recorded in Table 2.

Table 1. Values of the L*, a*, and b* coordinates by operators.

Day	Coordinate								
	L*			a*			b*		
	1	2	3	1	2	3	1	2	3
1	56.66	59.36	55.62	17.68	18.12	17.75	25.18	23.56	21.46
2	58.42	56.29	55.37	17.71	18.16	17.71	22.54	22.71	21.37
3	60.58	53.92	58.72	18.45	18.03	18.31	22.76	21.80	22.51

Table 2. F values calculated for the coordinates L*, a* and b*^a.

Day	Coordinate		
	L*	a*	b*
1	2.498	0.513	1.536
2	0.755	0.259	0.067
3	3.516	0.185	0.485

^a $\alpha=0.05$

Let k be the number of treatments and n the number of attempts made by the operators $k = 3$; $n = 3$. The horizontal and vertical degrees of freedom were determined by the following Equations $k(n - 1)$ and $k - 1$ [1]. We obtain $3(3-1) = 6$ vertical degrees of freedom and $3-1 = 2$ horizontal degrees of freedom; with these two values, the critical value of the F distribution tabulated as $f_{0.05}(2.6) = 5.143$ was determined. To corroborate the information the P-values were analyzed with respect to the data in Table 1, and the results are recorded in Table 3. The values in Table 3 show for each of the colorimetric variables that the P-values are more significant than 0.05.

From the information recorded in Table 2, it was determined that, for the first day of the test, the calculated F value corresponds to 2.498. This value is less than the tabulated F value, 5.143. These results indicate that the values of the L* coordinate (Luminosity) obtained in the enamel applications carried out are in the acceptance zone of the F distribution, and therefore it must be accepted that there are no significant differences in the values of the L* coordinate. The P-value corresponding to 0.162 in Table 3 confirms this result since it is greater than the α (0.05) value.

The same trend is observed for the second and third days of the test about the non-existence of significant differences by showing that the calculated F values are lower than the tabulated F values (Table 2). Furthermore, for the two days of testing, the calculated P-values are higher than the value of α (Table 3). This statement is verified as follows: for test days 2 and 3, the calculated F values are 0.755 and 3.516, respectively. These values are less than the tabulated F value that corresponds to 5.143. Observing the values corresponding to P-value, for days 2 and 3, it is evident in Table 3 that they are greater than the value of 0.05 corresponding to α .

Table 3. P-values for the coordinates L*, a*, b*^a.

Day	Coordinate		
	L*	a*	b*
1	0.162	0.623	0.289
2	0.510	0.780	0.936
3	0.098	0.836	0.638

^a $\alpha=0.05$

Figures 1, Figure 2, and Figure 3 show the box-and-whisker plots for each of the colorimetric coordinates. This type of diagram identifies outliers and compare distributions and knowledge in a comfortable and fast way of how 50% of the central values are distributed. The main advantages of representing the distribution of the data using this method are to visualize whether a variable's

distribution is skewed or away from the normal distribution. It facilitates the comparison of the distributions between the operator data.

Figure 1 shows the box plot for the L^* coordinate values recorded during the three days of testing. It is observed that the median and dispersion levels of operators 1 and 2 differ with those of operator 3, who presents the highest dispersion data; the boxes dimensions are determined by the distance of the interquartile range, which is the difference between the first and third quartiles. For the colorimetric coordinate L^* (Figure 1), it is evidenced that for operator 1, 50% of the data are between 56.2 and 60.3. For operator two, the range is 55.6 to 57.9, and operator three between 55.4 and 58.2. Concerning the median, it can be observed that the asymmetry is the flattering or right cut for the three operators. According to this behavior, the mean is greater than the median. The whiskers determine the limit for the detection of outliers. Figure 2 shows that the maximum length does not exceed 150% of the interquartile range for all operators. No outliers are observed.

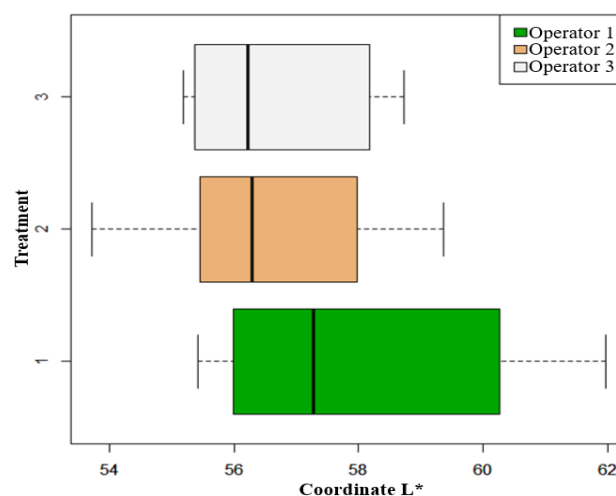


Figure 1. Comparison of medians obtained for the L^* coordinate.

For the coordinate a^* , it is concluded that there are no statistically significant differences for the three days of testing. These results are evidenced by the fact that the calculated F values are less than those of F tabulated, as shown in Table 2, and the P-values are more significant than the value of α . The values of F calculated for test days 1, 2, and 3 are 0.513, 0.259, and 0.185, respectively (Table 2). When comparing these values with the tabulated F value (5.143), it is evident that they are lower in the three cases of analysis. Verifying the P-values for days 1, 2, and 3 in Table 3, it is observed that they are less than 0.05, which corresponds to the value of α .

Figure 2 shows a box plot for the a^* coordinate values recorded during testing three days. It is observed that the median and dispersion levels are similar for the three operators. Outliers are recorded for operators 1 and 2. For the colorimetric coordinate a^* (Figure 2), the box-and-whisker diagrams show that 50% of the analyzed data are located. For operator one between 17.7 and 18.3. For operator two the range is from 18.1 to 18.3, and operator three between 18.0 and 18.4. For the median, it can be seen that the asymmetry is positive or right-angled for the three operators, and therefore, the mean is greater than the median. Regarding whiskers, it is evident in Figure 2, for operators 1 and 3 that the maximum length does not exceed 150% of the interquartile range. Outliers are observed in the data of operator-2, but they do not exceed 1.5 times the interquartile range, and therefore, the length of the whisker will be from the third quartile to the maximum.

For the b^* coordinate, the statistical study allows establishing the non-existence of statistically significant differences. This trend is observed in the measurements for the three test days. As mentioned above, this conclusion is supported by the information recorded in Table 2. This table shows that the

calculated F values are lower than the tabulated F values. The non-existence of a statistically significant difference is corroborated by P-values that are greater than the value of α . The statistical analysis allowed to establish that F's values for the three days of the test correspond to 1.536, 0.067, and 0.485, respectively (Table 2). Regarding the P-values, Table 3 shows that for the three days of testing, they are 0.289, 0.936, and 0.638, respectively.

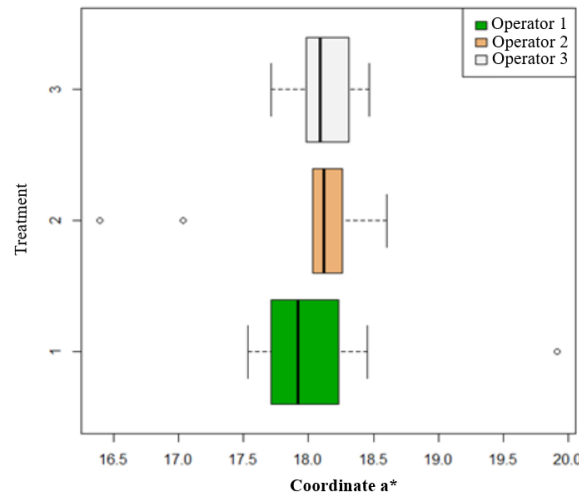


Figure 2. Comparison of medians obtained for the coordinate a^* .

Figure 3 shows the box plot for the b^* coordinate recorded values during the three days of testing. It is observed that the median and dispersion levels are similar for treatments 1 and 2, then atypical values are presented for treatment 3. For the colorimetric coordinate b^* (Figure 3), the box and whisker diagrams show that 50% of the data are located in ranges between 22.5 and 24.3 for operator 1. For operator two, the ranges between 21.9 to 23.9, and operator three between 21.9 and 22.5. With respect to the median, it can be seen that the asymmetry is positive or right-angled for the three operators, and therefore the mean is greater than the median. Regarding whiskers, it is evident in Figure 3, for operators 1 and 2 that the maximum length does not exceed 150% of the interquartile range. Outliers are observed in the operator 3 data but do not exceed 1.5 times the interquartile range.

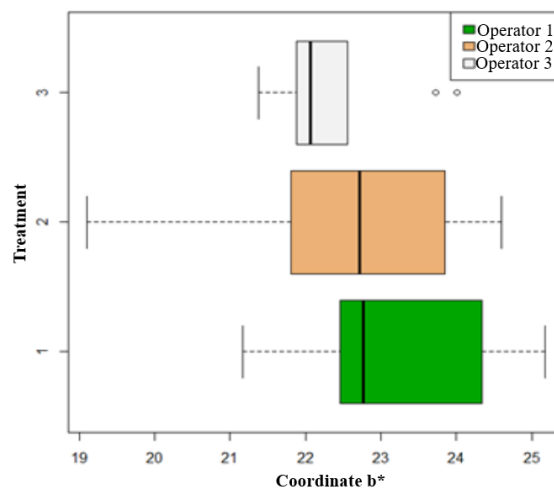


Figure 3. Comparison of medians obtained for the b^* coordinate.

4. Conclusions

The most important conclusion reached at the end of this work is that the value of the colorimetric coordinates L^* , a^* , and b^* does not present statistically significant differences as a product of the operator who performs the application because all the calculated F values are lower than the value $f_{0.05}(2.6)$. Therefore, there is no evidence of the influence of applying a ceramic enamel on the final quality of the finished product.

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