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Color prediction in ceramic enamels using the kubelka munk model

Predicción de color en esmaltes cerámicos aplicando el modelo de kubelka munk

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Abstract

In the present research, the Kubelka-Munk model was applied for predicting color in glazes used in ceramic decoration. The model relates the absorption coefficient, scattering coefficient and the diffuse reflectance expected for a mixture of three ceramic pigments in the visible spectrum. The concentrations of each enamel were also considered making possible predict a particular tone. It was used visible spectrophotometry to obtain the absorption and scattering coefficients of pigments chosen on ceramic substrates for their use in pottery, and also for the diffuse reflectance spectra of mixtures selected for burned enamels. The results showed a good prediction in some regions of the visible spectrum, concluding that the model could be used for quality control of products manufactured in the ceramic industry.

Keywords: Color prediction, Kubelka-Munk, ceramic enamel, ceramic pigment.

Resumen

En este trabajo se muestra la aplicación del modelo de Kubelka-Munk para la predicción de color en esmaltes utilizados en decoración cerámica. El modelo relaciona los coeficientes de absorción y de dispersión de reflectancia difusa esperados para una mezcla de tres pigmentos cerámicos en el espectro visible, con las respectivas concentraciones de la composición de cada esmalte, con lo cual es posible predecir un tono determinado. Se empleó espectrofotometría visible con el fin de obtener los coeficientes de absorción y dispersión de los pigmentos elegidos sobre sustratos cerámicos para locería y también para los espectros de reflectancia difusa de las mezclas elegidas para los esmaltes calcinados. Los resultados obtenidos mostraron una buena predicción en algunas regiones del espectro visible, concluyéndose que el modelo podría utilizarse para el control de calidad de los productos fabricados en la industria cerámica.

Palabras clave: Predicción de color, Kubelka-Munk, esmalte cerámico, pigmento cerámico

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1. Introduction

Color matching is defined as the methodology used in the colored products industry to predict and standardize the color of a material resulting from the mixture of pigments or dyes previously established [1]. In the manufacturing of plastics, printing, textiles and paintings, color prediction is a tool that has solved the problem of chromatic variations that arise between production batches [2].
Some of the advantages of color matching for manufacturing industries include the possibility to obtain a large number of tones combining a small number of pigments or dyes. These procedures could be advantageous when are applied to the ceramic industry, as has been proven for predicting color in ceramic glazes [3] [4] [5] [6] [7] [8] [9] [10]
The most used model in the industries of paint, paper, textile and plastic for color formulation has been the physical color model Kubelka-Munk [11]. This method uses the spectral reflectance in the visible region to predict the color of opaque materials. Reflectance is a function of the light absorbed and scattered by the particles of the pigment in the substrate [12]. Therefore, each component of a color formulation has an absorption coefficient *K*, and scattering coefficient *S*, which are wavelength dependent. In particular, when solid objects have thin layers, the relationship describing the theory of Kubelka Munk is as follows:

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$$\frac{K_\lambda}{S_\lambda} = \frac{(1-r_\lambda)^2}{2 * r_\lambda} \quad (1)$$

Where K_λ, S_λ and r_λ, are the absorption and scattering coefficients and diffuse reflectance percentage, respectively [13], [14]

Another important equation for color formulation was developed by Duncan [15], which shows the contribution of the absorption and scattering property as an additive a mixture of pigments, described by the following equation:

$$\frac{K_\lambda}{S_\lambda} = \frac{\sum_{i=1}^{n} C_n * K_{n(\lambda)}}{\sum_{i=1}^{n} C_n * S_{n(\lambda)}} \quad (2)$$

Where K_λ, S_λ and C_n are the absorption and scattering coefficients and the concentration of the pigment in the mixture at each wavelength λ in the visible spectrum [9]. In this way, the coefficients K_λ and S_λ for primary pigments of a basis set can be determined. Moreover, it is also possible to predict the resulting color from certain pigments mixture or determine pigment concentrations to reproduce a color from spectral measurements [5].

In this work, the Kubelka-Munk model is proposed for color matching purposes in ceramic enamels. Opaque glazes were prepared to determine the optical absorption constants for three primary pigments and frit suspension from the reflectance curves measured with a spectrophotometer.

2. Methodology

Ceramic enamels were prepared using a frit in suspension, three primary industrial ceramic pigments (blue, red and yellow) and ceramic substrates. Initially, three primary ceramic pigments were chosen, mixed with the frit suspension to make final calcination at a temperature of 1110°C. The samples were then characterized, measuring the diffuse spectral reflectance for each mixture of pigment and frit to obtain the absorption and scattering coefficients in the visible spectrum. From the coefficients and concentrations of the mix, the Kubelka Munk model was employed to calculate the expected color.

a. Formulation of ceramic enamels

Figure 1 shows the development of the mixtures of ceramic pigments, opacifier of zircon and industrial frit suspension for the ceramic enamel.

Table 1 Composition of the ceramic enamels

Sample	Frit suspension (% Weigth/Weigth)	Pigment (% Weigth/Weigth)			Opacifier (% Weigth/Weigth)
		Yellow	Blue	Red	
1	95	0	5	0	0
2	95	0	0	5	0
3	95	5	0	0	0
4	95	1	1	3	0
5	95	1	1	2	1
6	95	3	1	1	0
7	95	2	1	1	1

Figure 1 shows the blue, yellow and red ceramic pigments, together with the frit suspension and the ceramic substrate on which the ceramic enamel was applied.

The raw glazed pieces were dried at room temperature for 20 hours and then taken to an oven for firing using the thermal ramp shown in Table 2

Table 2 Thermal Ramp for firing enamels

Temperature (°C)	Time (minutes)
24 to 1100	180
1100	30
1100 to 25	Natural oven cooling

The relationship between the absorption and scattering coefficients K / S was obtained by diffuse UV-VIS spectrophotometry using a UV-VIS spectrophotometer Glacier X from BWTEK, with a spectral range from 200 nm to 1050 nm. A bidirectional geometry 45°: 0° was employed, and the light source was the CIE illuminant D65.

3. Results

Figure 2 shows the K/S ratio. It can be seen that the dispersion increased between 400 nm and 525 nm (S> K) with an absorption band between 575 nm and 700 nm (K> S). This band is associated with the electronic transitions of cation Co2+ ions in tetrahedral sites; likewise, the absorbed energy is dissipated by non-radiative processes. The pigment is a cobalt chromite ($CoAl_2O_4$) which shows a blue color due to the presence of the Co^{2+} ion in the spinel structure [16].

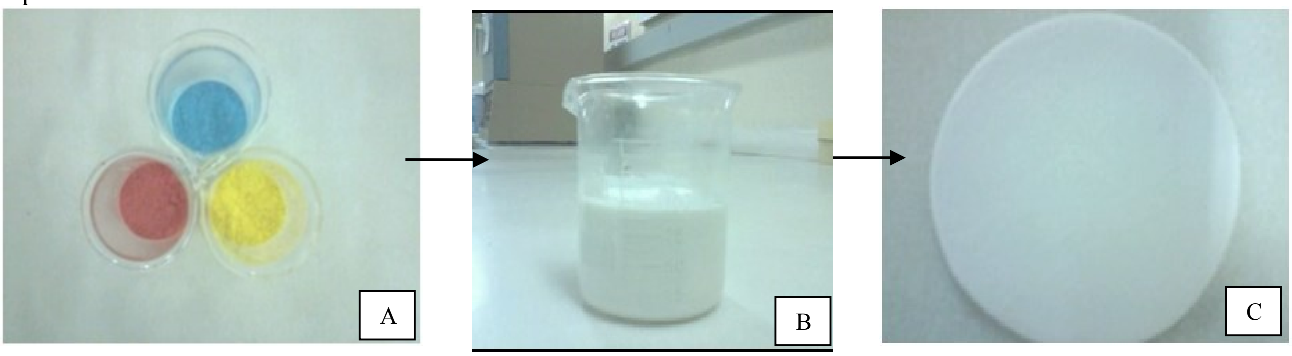

Figure 1 Preparation of ceramic enamels

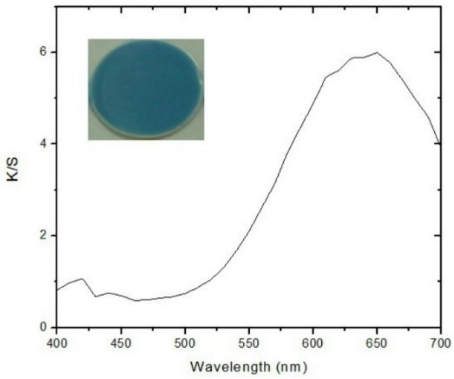

Figure 2 K/S ratio for the blue pigment in sample 1.

Figure 3 shows a broad absorption band between 400 nm and 600 nm that is associated with electronic transitions typical for cadmium red (CdSe) [17]. It is an n-type semiconductor material that the bandgap is about 1.74 eV at 300K.

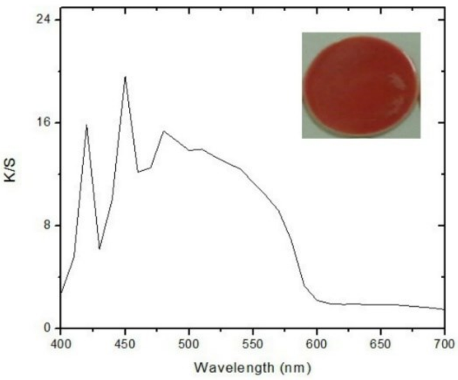

Figure 3 K/S ratio of the red pigment (sample 2).

Figure 4 shows low K/S ratio for yellow ceramic pigment (sample 3) in the region between 550 and 700 nm. This region is characteristic of a yellow pigment such as zircon praseodymium (Pr-$ZrSiO_4$) [18].

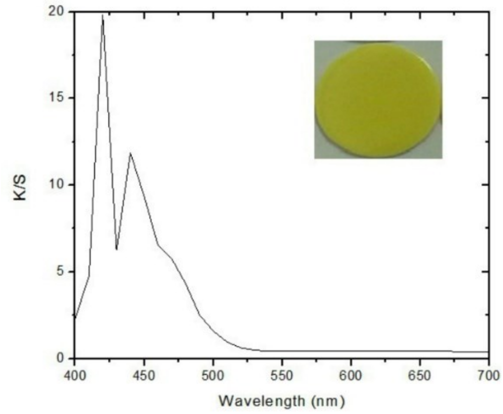

Figure 4 K/S ratio of the yellow pigment (sample 3).

Figure 5 shows the curves of experimental and theoretical diffuse reflectance of samples 4 and 5. A prediction of the shape of the curve is observed, but no suitable adjustment of the reflectance values, where the biggest difference is in the region of 450 to 550 nm. In an optical multicomponent system, all components must be considered. Usually, more emphasis is given to pigment, but in reality other optical system elements (frit and opacifiers) are equally important in determining optical properties enamel. In this study, only optical parameters K and S were taken into account for the pigments.

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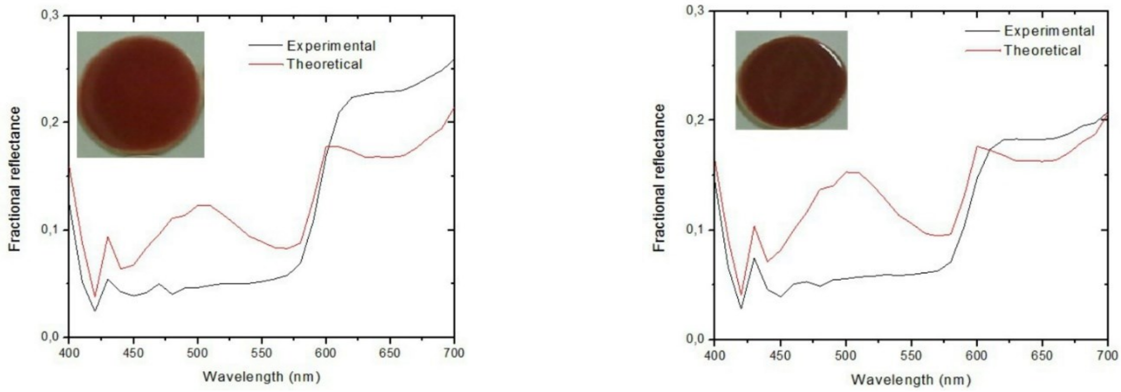

Figure 5 Experimental and theoretical diffuse reflectance sample 4 (left) and sample 5 (right).

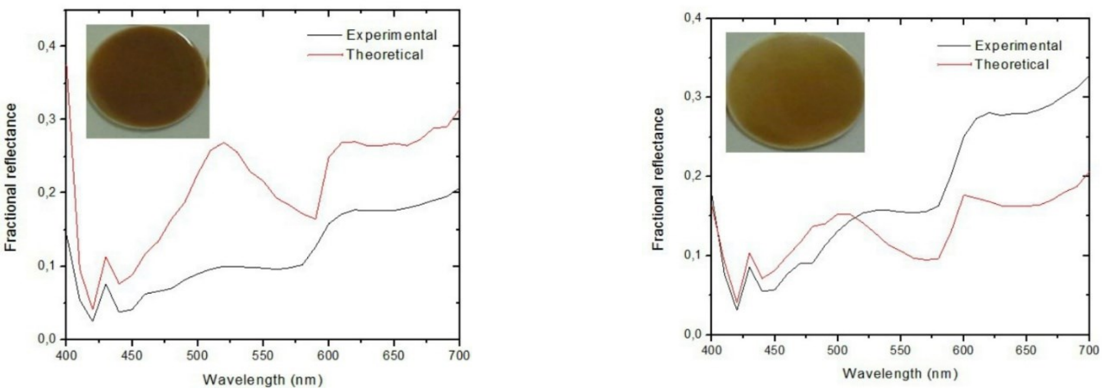

Figure 6 Experimental and theoretical diffuse reflectance of sample 6

Figure 6 shows the curves of experimental and theoretical diffuse reflectance of samples 6 and 7. A prediction of the shape of the curve is observed, but no suitable adjustment of the reflectance values, where the biggest difference is in the region of 450 to 550 nm. Similar to samples 4 and 5, it is important to consider the influence of all components in the calculation of the values of optical absorption K and optical dispersion S, as there may be interactions between the frit, opacifier, and pigments. Sample 7 has a good prediction in the low wavelength region, but no suitable adjustment of the reflectance values from 600 nm to 700 nm

4. Conclusions

Kubelka-Munk model for color prediction was effective for using in ceramic enamels with samples made up with three ceramic pigments as a color basis, in different regions of the visible spectrum. The experimental and the theoretical curves differ in some specific spectral regions by an order of magnitude due to the large amount of enamel used. This decreases the suitability of the model since it was developed for thin layers of non-glossy materials.

Despite differences, similarities in the shape of the curves suggest the model could be adapted to systems of glossy ceramic enamels using empirical measurements to minimize errors due to specular reflections. It would be very interesting to study the influence of the chemical composition of the frit and its interaction with pigments and opacifier in predicting color.

The ceramic pigments used were stable in the mix with frit suspension, presenting compatibility between enamel and pigment during firing, which is expressed through uniformity in the final color of the resulting sample.

The prediction color from diffuse reflectance measurements allows a great contribution to the technology of color, as it could get many tones from a combination of only three ceramic pigments.

Acknowledgments

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