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Color matching algorithms in ceramic tile production

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Abstract

In the present work, the possibility of transferring in the ceramic tiles production the know-how developed in the field of the paints by using the Kubelka–Munk theory, in the form used for opaque surface coatings, have been evaluated. Five different target colors have been chosen as target and tried to reproduce with an industrial glaze in a cycle for fine porcelain stoneware tiles. Four industrial pigments have been chosen as basic stains for the formulations. The results show a good efficiency of the color matching algorithm applied to pigments for glazes for fine porcelain stoneware tiles. All the formulations, in fact, have allowed to obtain a value of ΔE^* lower to the accepted limit.

Keywords: Pigment; Color; Tiles

1. Introduction

The utilization of algorithms in the formulation of colors is not a new idea in the industry. It has been approximately 50 years since the first colorant formulation algorithm was reported introducing the color matching concept. By color matching, we mean the ability to reproduce, through mixing few fundamental pigments, whatever type of color experimentally measured by using algorithms of calculus. In activities such as printing, the textile industry, plastics or cold paints,[1] this technique represents a working tool, long consolidated and efficient in supplying rapid solutions to many of the chromatic problems of the production process, both those of a formulating and qualitative nature. The advantages are the possibility to have an elevated number of colors using a low number of pigments, the rejects elimination in the pigment production because the color matching equipment can prepare in real time the required volume of mixtures, the possibility to replicate colors also if it is not available the pigment with the target color, the possibility to adjust errors in the preparation of the color, etc. These aspects should be certainly advantageous also in the ceramic field where many producers now use different typology of applicators (flat, drum, rotary with photoincisive rollers serigraphic machines) that in many plants frequently cohabit. All these factors normally leads to use a wide range of decorating materials (often a question of hundreds of colored products) that make up a complex system to manage both at a warehouse and production level. However, despite various attempts (studies intended to predict the color of a ceramic glaze can be found with interesting results in literature),[2–5] in ceramic tiles sector the technology of colorant formulation via software has not found a fertile field. For the final result, in fact, some specific limitations, characteristics of a ceramic material that develops its color during firing, have to be considered. The most important is connected with the thermal and chemical stability that pigments must have towards the molten glass (frits or sintering aids) developed during the firing cycle at high temperatures: the same pigment, in fact, can develop slightly different colors depending on both firing temperature and chemical composition of glaze or ceramic body to color. Aspects such as the grain size distribution, the chemical and physical interaction between pigments and glazes, variations during the firing process, the final appearance of the ceramic tile surface, make up a series of elements that

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influence in a determining way not easily controllable the development of colors.

In the present work, the possibility of transferring in the ceramic tiles production the know-how developed in the field of the paints by using the Kubelka–Munk theory, in the form used for opaque surface coatings, have been evaluated. Five different target colors have been chosen as target and tried to reproduce with an industrial glaze in a cycle for fine porcelain stoneware tiles. Four industrial pigments have been chosen as basic stains for the formulations. Moreover, the influence of the temperature on the efficiency of the algorithm has been evaluated.

2. Kubelka–Munk theory

All the most modern formulation softwares are essentially based on the application of the Kubelka–Munk theory (1931),[6] the most widely used in most industrial sectors. In measuring reflected color the values obtained for every wavelength are function both of absorbed light and scattered light by pigment particles.[7,8] This means that for every frequency of the visible spectrum, every component of a formulation possesses a coefficient of absorption, K, and a coefficient of scatter, S. In particular, when the layer of the absorbing-scattering material is so thick that no light penetrates through the layer (opaque surfaces), the relationship describes the Kubelka–Munk theory, taking into account also the Saunderson correction,[9] is given by:

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

where r_λ is the decimal fractional reflectance ($0 < r < 1$) measured at the wavelength λ with the specular component excluded.

Many modern spectrometers have the capability to measure the r parameter directly. However, if the available spectrometer can measure only total reflectance, this quantity can be estimated by the Saunderson correction:

$$r_\lambda = K_1 + \frac{(1 - K_1)(1 - K_2)R_\lambda}{1 - K_2 R_\lambda} \tag{2}$$

where R_λ is the decimal fractional total reflectance ($0 < R < 1$) measured at the wavelength λ; K_1 the coefficient of specular reflexion; and K_2 the coefficient of internal reflexion.

With this correction, the influence of the material–air interface on the reflectance measurement, not considered in the Kubelka–Munk theory, can be evaluated. In particular for a glaze surface, K_1 is the Fresnel reflection coefficient ($K_1 = 0.04$) while the internal reflexion coefficient, K_2, as determined experimentally, can be approximated to 0.4. The Eq. (2) becomes:

$$r_\lambda = \frac{R_\lambda - 0.004}{0.96 - 0.4(1 - R_\lambda)} \tag{3}$$

Another important equation for color matching, developed by Duncan,[10] demonstrates the additivity in a mixture M of the absorption and diffusion contributions of each component:

$$\frac{K_\lambda}{S_\lambda} = \frac{\sum c_n K_{n(\lambda)}}{\sum c_n S_{n(\lambda)}} \tag{4}$$

where c_n is the fractional concentration ($0 < c_n < 1$) of the n-th pigment in the mixture; $K_{n(\lambda)}$ the absorption coefficient of the n-th pigment in the mixture at the wavelength λ; and $S_{n(\lambda)}$ the scattering coefficient of the n-th pigment in the mixture at the wavelength λ.

To make use of this theory, one needs a straightforward way to obtain these coefficients from measurable reflectance data. In particular knowing these coefficients for all the components of a mixture it is possible to obtain the reflectance value, and thus the color, that it can be developed by a mixture, changing the components concentration. In fact:

$$R_\lambda = 1 + \frac{K_\lambda}{S_\lambda} - \left[\left(\frac{K_\lambda}{S_\lambda}\right)^2 + 2\frac{K_\lambda}{S_\lambda}\right]^{1/2} \tag{5}$$

where for the Saunderson correction for an opaque glaze surface, $R_\lambda = r_\lambda/(0.576 + 0.4r_\lambda)$ with r_λ decimal fractional reflectance ($0 < r < 1$) measured at the wavelength λ with the specular component excluded.

However, in order to determine the coefficient of absorption, K, and the coefficient of scatter, S, for all the components in a mixture it is necessary to introduce a series of approximations.

When the coating is opaque, the parameters K and S can be calculated setting arbitrarily to unity at every wavelength the value of the scattering parameter, S, of the white component. In this way, the absorption coefficient, K, of the white component is determined simply from a reflectance measurement of the white at complete hiding.

In this sense, the Eq. (1) for a white color becomes:

$$\frac{K_{w(\lambda)}}{S_{w(\lambda)}} = K_{w(\lambda)} = \frac{(1 - r_\lambda)^2}{2r_\lambda} \tag{6}$$

where $K_{w(\lambda)}$ is the absorption coefficient of the white pigment at the wavelength λ; and $S_{w(\lambda)}$ the scattering coefficient of the white pigment at the wavelength λ.

All other K and S values can be related to this. In particular, the coefficients of other pigments could be calculated using different procedures.

Eppler et al.[2–5] demonstrated that the individual K and S values for a given pigment constituent in a glaze can be obtained from measurements of the reflectance values in the given base glaze for a masstone of that pigment, a known letdown with opacifier, and the opacifier alone, all at the same total concentration of pigment plus opacifier in the glaze. The reflectance of the three pieces is then measured and, for any frequency, the K/S values are calculated for the pigment, the opacifier and the letdown by Eq. (1).

In this way, from known parameters it can be calculated:

$$S_P = \frac{c_w}{c_P}\frac{(K/S)_{LD} - K_w}{(K/S)_P - (K/S)_{LD}} \quad \text{and} \quad K_P = \left(\frac{K}{S}\right)_P S_P \quad (7)$$

In this work, instead, we use the Davinson and Hemmendinger Method[11] that operatively consists in these successively steps:

(1) determining the optical constant K for the white set S equal to unity at all wavelengths;
(2) prepare a mixture with blak and a masstone (100% relative percentage pigment). Solve Eq. (4) by substitution of the value for K/S from Eq. (1);
(3) prepare a mixture of the pigment with white and also a masstone of the pigment and compute K and S as in the step (2);
(4) prepare a mixture with a small amount of black. Solve Eq. (4) for mixture with black by substituting the values for K and S for the black determined from step (2) and the values for K/S for the pigment determined from Eq. (1);
(5) select the values for K and S in the absorption region from step (3) and the values for K and S in the scattering region from step (4), shifting from one set of data to the other at the point where the two set are very similar.

There are several reasons for using the complex Davinson–Hemmendinger method rather than the easier method used by Eppler. First of all the evidence that the accuracy with which the S coefficient of a pigment can be computed when in mixture with highly scattering white pigment, is poor. Moreover the fact that the assumption that the scattering and absorption coefficients are constants over the entire range of concentration and loading is, in certain cases, not valid.[7]

3. Experimental

Four industrial pigments have been chosen as basic stains for the formulations (Table 1). The pigments have been chosen according to their intensity, tone purity, stability to both the firing temperature and chemical aggression exerted by the chosen glaze. A white industrial zirconium silicate has been used as opacifier, while the black pigment is a commercially available iron–chromium pigment. The base glass has been an industrial frit for high temperature (Table 2).

Table 1
Pigments and opacifier utilized

Pigment	Composition	Product used[a]
Yellow	$(Zr,Pr)SiO_4$	PG 160
Coral	Fe_2O_3–$ZrSiO_4$	PG 240
Blue	$CoAl_2O_4$	PG 10
Green	$(Cr,Al)_2O_3$	PG 78
Black	$FeCr_2O_4$	PG 116
White	$ZrSiO_4$	Zircobit

[a] All Colorobbia–Italia products.

Table 2
Composition of the used glaze (Colorobbia–Italia)

Oxide	Amount (wt.%)
Na_2O	0.93
K_2O	1.03
CaO	12.4
MgO	10.4
Al_2O_3	11.8
SnO_2	0.7
SiO_2	61.95
Fe_2O_3	0.3
TiO_2	0.46

3.1. Calibration curves construction

For each pigment a calibration curve, which is used to form the operative database of the formulation software has been built up. K and S parameters have been determined preparing the following five mixtures: three with different percentage of glass, pigment and white opacifier, one where the white opacifier has been replaced with a black pigment, one in which neither opacifier neither black pigment has been added (masstone). In all the samples, the same amount of sodium bentonite has been added (2 wt.%).

The obtained glassy suspension has been deposited on a fine porcelain stoneware tiles 2–3 mm in thickness to obtain the complete coverage and has been fired with a industrial firing cycle (T_{max} = 1220 °C, total firing time = 45 min). The reflectance spectra of the samples after firing have been measured by COLORLAB Ver. 4.5 UV–vis. Spectrophotometer (CPS Color) and the K and S values have been determined by the CorobWorld Ver. 2.0 software (CPS Color), which uses the Davinson–Hemmendinger method.

3.2. Tests of color matching

Five different target colors (yellow, green, blue, brown and gray) in the NCS standards (*Natural Color System*, Edition 2, Scandinavian Color Institute, Stockholm) have been chosen in order to experimentally verify the obtained calibration curve and the D–H model. They have been analyzed by the UV spectrophotometer and hypothetical formulations based on the characterized pigments have been calculated utilizing the software CorobWorld Ver. 2.0. The target colors have been reproduced in laboratory adding the obtained pigment formulations to the glassy system and firing with the same heating cycle used to characterize the pigments. The reflectance spectra successively measured on the so-obtained samples have been compared with the spectra of the NCS standards.

Finally, to study the influence of the firing temperature on the color matching, two colors, the yellow and the blue, have been prepared using the same procedure utilized previously

and fired at different temperatures (1140–1160–1180–1200 –1250 °C) in a laboratory kiln. The reflectances have been measured and confronted with that of the references.

4. Results and discussion

In the present work, the term "masstone" is used for the mixture: pigments (10 wt.%), glass (88 wt.%) and sodium bentonite (2 wt.%). The K and S parameters have been determined for the system "masstone" and likewise the formulation to reproduce the NCS standards have been determined considering the mixtures. In this way, we have tried to avoid the correction suggested by some authors[3] due to the solubility of the pigment in the glass that determines a reduction of the pigment tint strength.

The ratio K/S for the colors after firing is plotted versus wavelength in Fig. 1. The opacifier shows very low values because the absorbed light is limited, independently by the value of S assumed equal to 1. On the contrary, black and blue have the highest ratio K/S in consequence of the low portion of scattered light.

In Fig. 2, the reflectance versus wavelength for the first color obtained using the color matching is presented. In particular, the graph shows the curves of both the yellow NCS standard S-0550-G90Y and the corresponding formulation prepared using the pigments previously characterized. The agreement between the two spectra is good, as it is also demonstrated by the low value of ΔE^*, based on the relationship:

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \quad (8)$$

where ΔL^*, Δa^* and Δb^* measure the differences in luminosity and in chromaticity with respect to standards (CIELab method).[12] Thus, if Δa^* is positive, the sample is redder than the standard; if negative, it is greener. And if Δb^* is positive, the sample is yellowier than the standard; if negative, the sample is bluer than the standard.

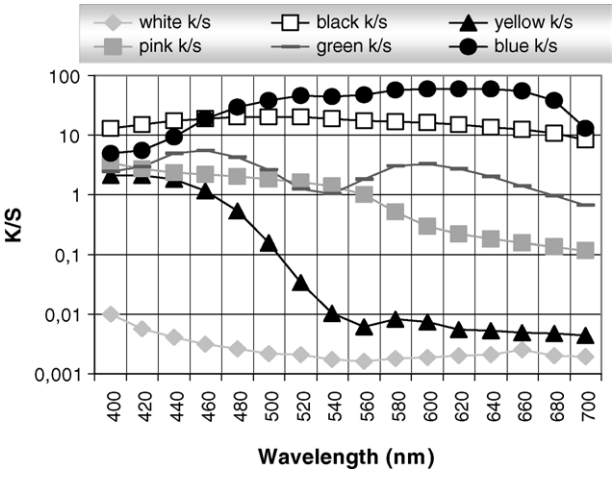

Fig. 1. K and S parameters for the pigments and opacifier utilized to standardize the color matching procedure (typical firing cycle of fine porcelain stoneware tiles, masstone mixture).

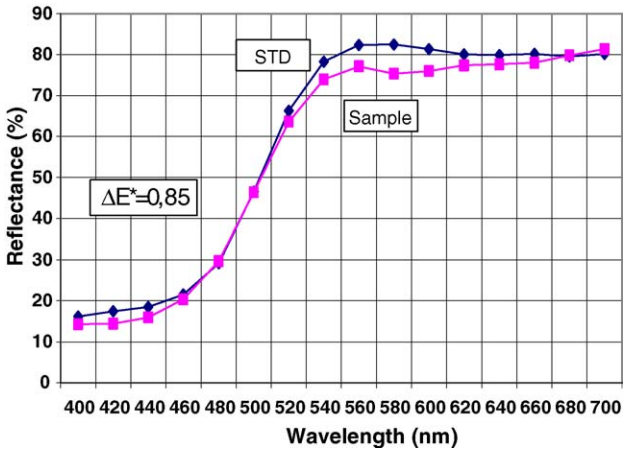

Fig. 2. Reflectance spectrum of the yellow NCS standard S-0550-G90Y (STD) compared with that obtained by color matching (Sample).

In the field of the wall paint, where a high precision in the color reproduction is required, the limit of acceptability of ΔE^* is between 0 and 1.5. As the value obtained for the yellow is inside this limit, it is possible to consider positive the result.

A significant test has been carried out on a gray NCS standard S-3010-R90B. This color is particularly difficult to reproduce with color matching because also little variation in the formulation determines big differences in the final result. In Fig. 3, the reflectance curves of the standard and the sample obtained after the color matching are shown. A good agreement has been obtained as confirmed by the low value of ΔE^*. In Fig. 4, the spectrum of the blue NCS standard S-7010-R70B is plotted together with the reflectance of the formulation obtained by the color matching. The curves present

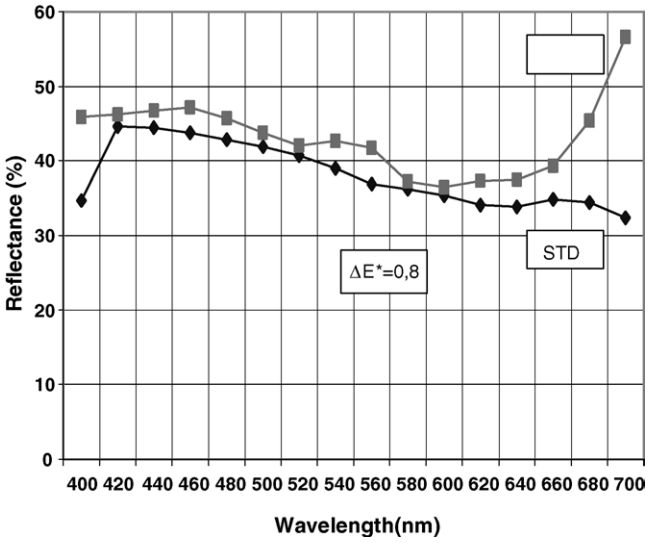

Fig. 3. Reflectance spectrum of the gray NCS standard S-3010-R90B (STD) compared with that obtained by color matching (Sample).

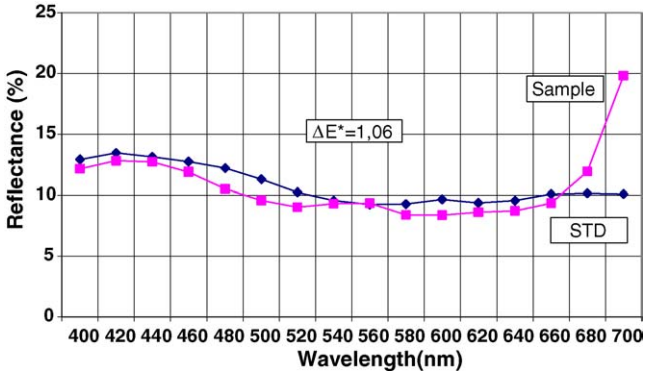

Fig. 4. Reflectance spectrum of the blue NCS standard S-7010-R70B (STD) compared with that of the formulation obtained by color matching (Sample).

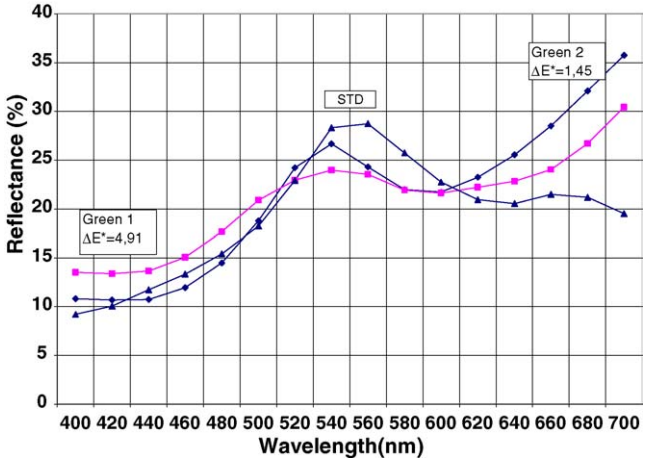

Fig. 5. Reflectance spectrum of the green NCS standard S-4030-G50Y (STD) compared with that of the formulations obtained by color matching (Green 1 and Green 2).

a good agreement and a ΔE^* close to 1. In Fig. 5, the spectra of the green NCS standard (S-4030-G50Y) and two different calculated formulations (Table 3) are plotted. As known, the green color can be obtained mixing yellow and black, but the result is often not satisfactory and it is better to introduce in the formulation a green pigment. In fact, black produce a darker color and the addition of yellow is not sufficient to increase the brightness of the final results. For the sample Green 1 (yellow + black), in fact, the ΔE^* value is out of the limit, while it is close to it for the sample Green 2. Finally in Fig. 6, the results obtained for the brown standard NCS S-2020-Y30R are shown. The agreement between the

Table 3
Calculated formulations to reproduce the green NCS standard (S-4030-G50Y)

Formulation	Green 1	Formulation	Green 2
White	0.173	White	3.09
Black	2.19	Yellow	52.91
Yellow	66.21	Pink	9.16
Green	1.00	Green	4.53
ΔE^*	4.91	ΔE^*	1.45

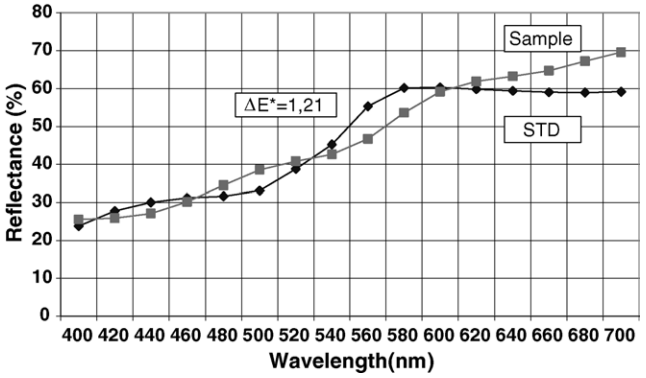

Fig. 6. Reflectance spectrum of the brown NCS standard S-2020-Y30R (STD) compared with that of the formulation obtained by color matching (Sample).

two reflectance curves is good and the ΔE^* is well inside the acceptability range.

The obtained satisfactory results do not seem to point out a negative action of the bentonite on the color matching. The sodium bentonite is commonly introduced inside the glaze slurry, about the 2–3% by weight with respect to the solid phase, with the purpose to reduce the sedimentation rate of the solid particles. The percent of the 2% in weight does not induce anomalies in the calculus of the mixture formulation.

Finally in Figs. 7 and 8, the temperature influence on the yellow and blue colors development is shown. They present an opposite behavior: the yellow glaze increases its whiteness with increasing temperature while the blue glaze increases its darkness. This phenomenon is pointed out by the color matching. The samples re-formulated with color matching algorithm show a theoretical composition where the ratio white/yellow increases with the increasing of the temperature while the ratio white/blue decrease. The result appears of sure interest and suggests the possibility to use the color matching in order to correct variations of tone produced by a firing curve modified with respect to the original. This problem is quite common in a plant when it is necessary to reproduce a color after many months or after a kiln firing curve change.

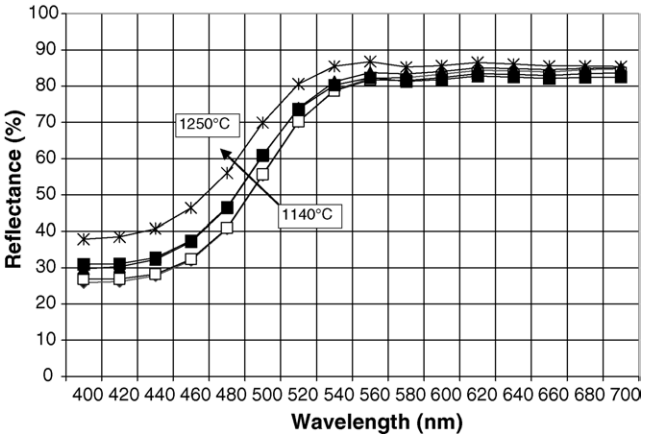

Fig. 7. Temperature influence on the developing of yellow coloration.

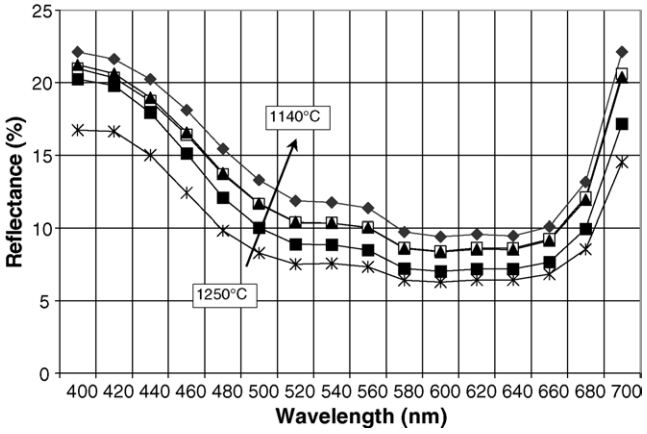

Fig. 8. Temperature influence on the developing of blue coloration.

5. Conclusion

The results show a good efficiency of the color matching algorithm applied to pigments for glazes for fine porcelain stoneware tiles. The decisive steps have been the introduction of a base glass in the formulations and the characterization of the colored glazes after firing. The color matching experiments have been conducted on five target colors and the determined formulations have allowed to obtain, after firing, results very close to the targets. All the measured ΔE^*, in fact, are lower to the acceptability limit. The effect of the temperature on the final color after firing is in agreement with the results of the color matching, so the way to correct color differences due to temperature variations, that inevitably happen in a industrial kiln in time, could be practicable.

In the evaluation of the results, it is necessary to consider also the reduced number of pigments utilized and that an increment in their number could improve the final result. In any case, the availability of a higher number of pigment is preferable both to obtain colors closer to the target and mixture more advantageous from a economic point of view.

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