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Colouring of opaque ceramic glaze with zircon pigments: Formulation with simplified Kubelka–Munk model

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Abstract

In this study a simplified Kubelka–Munk model is proposed for colour matching purposes. Opaque glazes were prepared to determine the absorption optical constants from the reflectance curves measured with a spectrophotometer. After the physical and chemical characterization of the glaze components (frit and pigments), to analyze the spectrophotometric results a simplification of the Kubelka–Munk model was suggested. To experimentally verify the model, two target green colour were reproduced in laboratory by adding in an opaque glaze a yellow praseodymium-doped zircon ($(Zr,Pr)SiO_4$) and blue vanadium-doped zircon ($(Zr,V)SiO_4$) pigments. The results were in good agreement with the experimental reflectance curves and the prediction of colour green glazes was possible with a reduced number of experiments.

Keywords: Spectroscopy; Colour; Optical properties; Traditional ceramics

1. Introduction

The prevision or formulation of colour using calculation software (colour matching) is one common practice in many industrial sectors. It is very popular in textile and paint sectors and recently is becoming known and consolidated also in the major part of ceramic industries.[1] In these softwares the prevision method is based on the Kubelka–Munk model[2] that correlates the colour with the added pigment concentration facilitating the formulation step. In particular, the model relates the reflectance with the properties of light absorption and light scattering of the pigments added to mixture.[3,4] In this context, also for ceramic glazes, both the colour formulation and control can be quite simple with the aid of theses softwares. Moreover, a more rationalized use of pigments can be achieved.

The Kubelka–Munk model relates the reflectance (R) to the absorption (K) and scattering (S) of light by the equation:

$$\frac{K}{S} = \frac{(1-R)^2}{2R} = F(R) \tag{1}$$

where R is the fractional reflectance, K is the absorption coefficient, S is the scattering coefficient at each wavelength of light in the visible region (400–700 nm). This simple relationship can be applied to thick opaque plastics, to paints with a complete hiding and to opaque ceramics.[5] Duncan[6] demonstrated the additivity of the individual contributions of absorption and scattering in a mixture, M, at each wavelength:

$$F(R) = \left(\frac{K}{S}\right)_M = \frac{c_1K_1 + c_2K_2 + c_3K_3 + \cdots}{c_1S_1 + c_2S_2 + c_3S_3 + \cdots} \tag{2}$$

where K/S is the light absorption caused by a mixture of pigments; c_i refers to the fractional concentration of the pigments added to the formulations; K_i and S_i are, respectively, the absorption and scattering coefficients and R is the reflectance measured by a spectrophotometer. When the K_i and S_i values are calculated at each wavelength in the visible region for the i pigment, the relation K/S of the mixture can be predicted and consequently the reflectance (colour) of the mixture.

In the ceramic industry one of the mean goal in the application of a glaze is to improve the aesthetic of the finished product. In this context the colour is essential and thus understand

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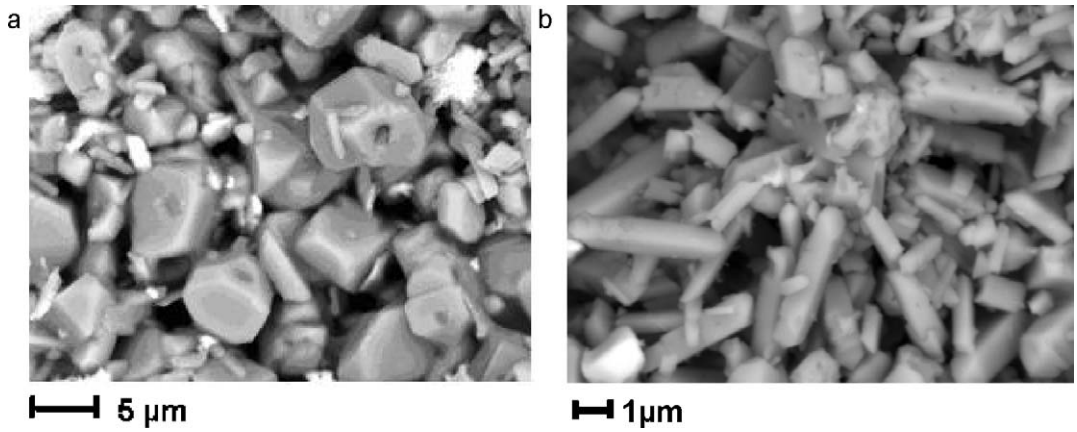

Fig. 1. SEM micrograph of the zircon pigments used. (a) Blue zircon–vanadium; (b) yellow zircon–praseodymium.

the contribute of the different mixture components (pigments, opacifier and glaze) on the final proprieties of light absorption and light scattering is fundamental to control the ceramic appearance.[7–9]

The reflectance (colour) of ceramic glazes is influenced by the grain size distribution and by the refraction index of both pigment and vitreous phase. The larger the difference between these refraction indexes, the larger the phenomenon of matting. The most currently used opacifier is zircon ($ZrSiO_4$). It have an high refraction index (1.96) and is considerably less expensive than titanium dioxide, also very used as opacifier.[9,10] Opacity and whiteness in ceramic glazes are generally obtained through crystallization of zircon from ZrO_2 and SiO_2 in the frit. The resulting micro heterogeneities (<10 μm size) have a significantly higher index of refraction than the glassy matrix (1.50–1.70) and thus effectively scatter light.[8] In fact the Mie scattering calculations[9] identify that, in an ideal system, the maximum light scattering and whiteness with zircon occur with a particle size range of 0.60–0.75 μm and a mass fraction of 0.16.[9,11]

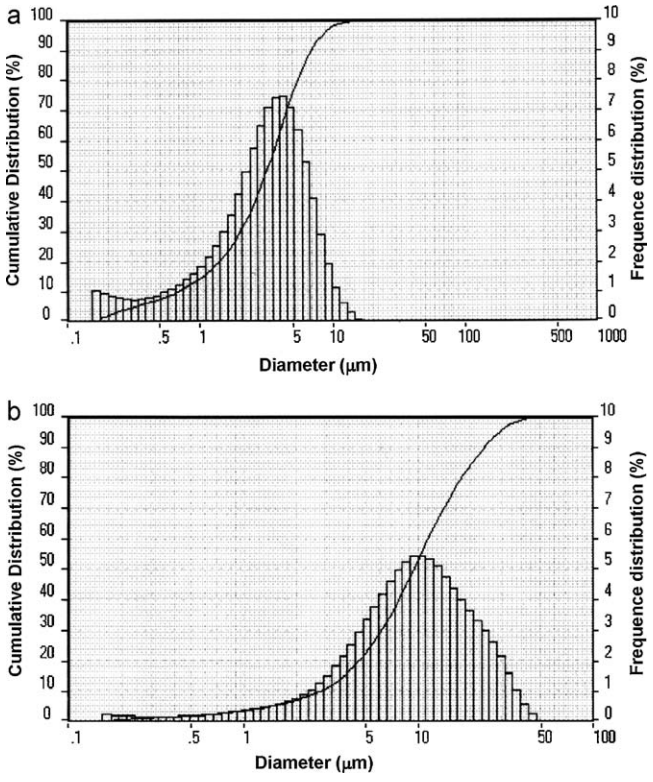

Fig. 2. Grain size distribution of the pigments. (a) Yellow zircon–praseodymium; (b) blue zircon–vanadium.

Zircon-doped pigments are the most stable ceramic colorants up to ∼1200 °C. Zircon tetragonal structure, that has the ability to accommodate substitutionally different colouring metals, i.e. vanadium and praseodymium, is characterized by high chemical and thermal stability that make it ideal for use in ceramic coatings. For this reason the zircon triaxial system is commonly used to colour industrial glazes. It is based on blending zircon–vanadium blue, zircon–iron coral, and zircon–praseodymium yellow to obtain a wide range of colours. Zircon pigments are normally added to glaze batches in range of 0.1–5.0% by weight, and their solubility change during firing with the melt composition.[8]

Moreover, to study the optical behavior of a glaze it is important to understand the physical interactions between the pigments, the opacifiers and the glaze. The optical properties of an object depend on the energy distribution at every wavelength (reflectance) that is function of the absorbed and scattered light. This means that for each frequency in the visible all the components of the glaze (pigments, opacifiers and, eventually, crystals devitrified from frit) have both an absorption and scattering coefficient, each one contributing to the optical properties of the glaze. For this reason in such multicomponent optical system it is important to consider all components. Normally the major emphasis is placed on the pigments, even if to the determination of a colour, the other optical elements of the system (opacifiers and the crystalline phases eventually crystallized during firing with refractive index higher than that of the vitreous phase) are equally important.[9] To complete this panorama it is important to underline that in the ceramic glazes the hue variations can be caused also by process variables,[12] e.g., firing temperature or grain size distribution that can affect the pigment and opacifier dissolution rate.[13]

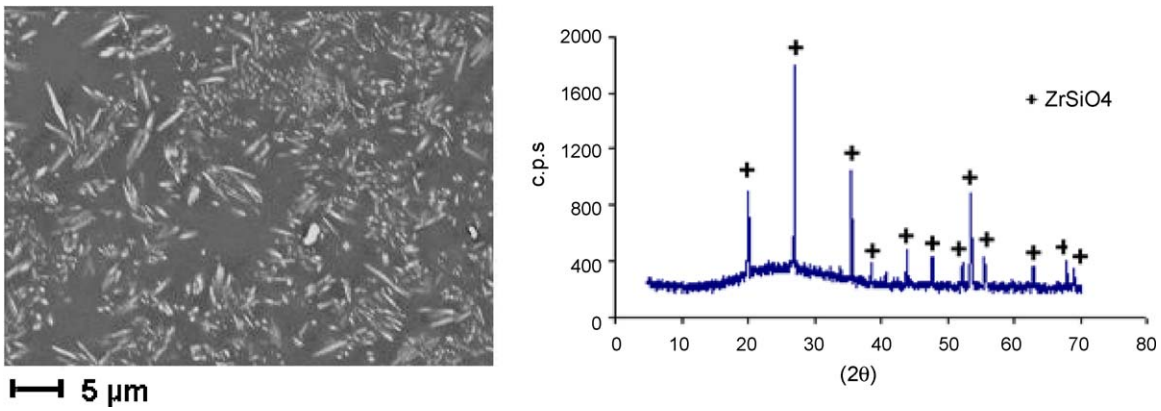

Fig. 3. SEM micrograph and X-ray diffraction pattern of the glaze after firing.

Aim of this study was to evaluate the possibility to simplify the Kubelka–Munk model in the prediction of the green colour developed by blue and yellow zircon pigments in an opaque ceramic glaze taking into account all the optical elements of the system. In particular the use of a simplified model was possible because of the peculiarity of the studied system.

2. Simplification of the Kubelka–Munk model

The Kubelka–Munk model previously shown is known also as "two constants model", because for each component of the system is necessary to determine the two constants K and S.

In this work a simplification of the Kubelka–Munk model was possible due the peculiarity of the studied system. The chosen opaque glaze contains a frit that during firing devitrifies zircon crystals that induce the light scattering: in this case the glaze can also be considered as one component of the mixture in the Kubelka–Munk model. Furthermore if both the used pigments and opacifier are based on zircon structure the model becomes[14]:

$$\left(\frac{K}{S}\right)_M = \frac{c_g K_g + c_p K_p + c_o K_o}{c_g S_g + c_p S_p + c_o S_o} = \frac{(1-R)^2}{2R} \tag{3}$$

where the subscripts g, p and o refer to glaze, pigment and opacifier respectively. Taking into account that the zircon crystals both crystallized in the glaze and added as opacifier and pigments have the same refraction index ($S_g = S_o = S_p = 1$), the Kubelka–Munk model for these mixtures can be semplified[14]:

$$\left(\frac{K}{S}\right)_M = c_g K_g + c_p K_p + c_o K_o \tag{4}$$

becoming a "one constant (K) model".

Consequently, to determine the coefficients of Eq. (4) is necessary to measure the reflectance and calculate the K/S ratio using only three samples: one sample prepared only with the glaze (to determine K_g), one sample with a fixed percentage of opacifier (to determine K_o) and one sample with a fixed percentage of pigment (to determine K_p). The total load added in the glaze must be the same in all the samples.[14]

Fig. 4. Image of the glazes after firing.

In particular, the reflectance measured on the sample formed by glaze and opacifier permits to calculate $(K/S)_{go}$, and thus to obtain K_o by the expression:

$$K_o = \frac{(K/S)_{go} - c_g K_g}{c_o} \tag{5}$$

where c_g and c_o are the concentrations of the glaze and opacifier, respectively.

The reflectance measured on the sample formed by glaze and pigment can be used to calculate $(K/S)_{gp}$ and to obtain K_p by the expression[14]:

$$K_p = \frac{(K/S)_{gp} - c_g K_g}{c_p} \tag{6}$$

Hence, all parameters of Eqs. (5) and (6) (K_g, $(K/S)_{go}$ and $(K/S)_{gp}$) are measurable (calculated from the reflectance data of the three samples) and the absorption coefficients (K_p and K_o) can be determined.

Finally, Eq. (4) can be used for the colour prediction of ceramic glazes in function of concentrations of zircon pigments and opacifier. When none opacifier is added and a mixture of zircon pigments is used Eq. (4) can be written as:

$$\left(\frac{K}{S}\right)_M = c_g K_g + c_{p1} K_{p1} + c_{p_2} K_{p_2} + \cdots \tag{7}$$

where p_1 and p_2 refer to the several zircon pigments added.

Table 1
Concentration of zircon pigments in the prepared glazes and respective colorimetric data.

	wt% zircon–V	wt% zircon–Pr	L^*	a^*	b^*
Glaze	–	–	96.0	−0.87	2.55
Yellow glaze	–	5.0	91.0	−3.4	44.9
Blue glaze	5.0		77.3	−8.8	−17.6
Green glazes	1.75	3.25	78.7	−11.6	14.9
	1.50	3.50	79.7	−10.8	16.26

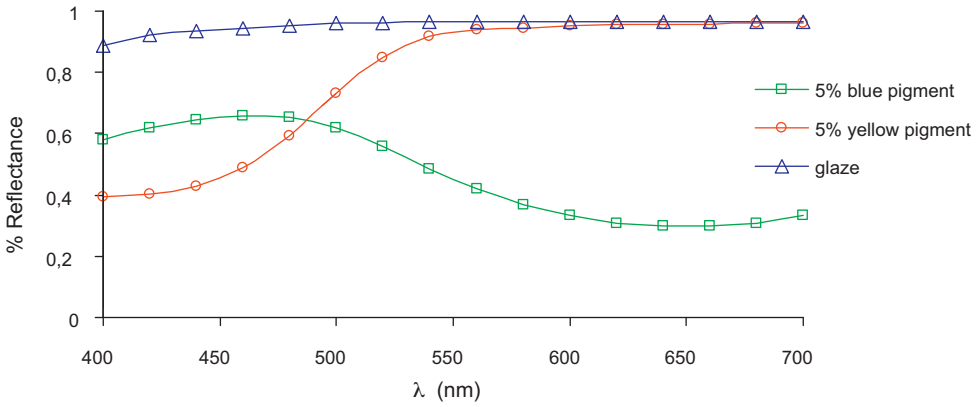

Fig. 5. Reflectance of the three glazes prepared for the determination of Kubelka–Munk coefficients.

3. Experimental procedure

In this work green glazes were prepared using two industrial micronized zircon pigments (Ferro Ltda.), the yellow zircon–praseodymium ($(Zr,Pr)SiO_4$) and the blue zircon–vanadium ($(Zr,V)SiO_4$). In the glazes preparation grain size distributions (pigments) and firing temperature were carefully controlled to avoid possible hue variations due to these process variables.[12–14] These pigments were characterized by X-ray diffraction analysis (XRD, PW 3710, Philips Research Laboratories) and by scanning electron microscopy (SEM, XL 30 Philips) equipped with an X-ray energy dispersion spectroscopy (EDS, INCA). Their grain size distributions were measured with a laser granulometer (Fritsh, model Analysette 22). The used frit was a typical zircon opaque frit[4] that during firing devitrifies to form zircon crystals, $ZrSiO_4$, as verified by scanning electron microscopy and X-ray diffraction. For the determination of the Kubelka–Munk constants (K_{p1} and K_{p2} in Eq. (7)) two pigmented glazes were prepared in a laboratory ball milling with: 87.5 wt% opaque frit, 7.5 wt% kaolin and 5 wt% of pigments as reported in Table 1. The powders were wet milled with water (1:1 powder to water ratio) and successively dried in oven at 120 °C. A glaze without pigments was also prepared. The total quantity of pigment added in the glazes was fixed at 5 wt%. Cylindrical samples (25 mm diameter and 6 mm thickness) of glazes were prepared with a laboratory press with 6 wt% water. The samples were fired in semi industrial kiln at 1175 ± 10 °C for 40 min. The reflectance curves and the L^*, a^*, b^* parameters of the samples were obtained with a spectrophotometer (Model Datacolor Spectraflash 600) using the optical geometry $d/8$, illuminant $D65$ and observer 10°. The microstructure of the glazes was determined by SEM in order to verify the dispersion of the pigments in the glaze.

Finally, to evaluate the efficiency of the prediction of simplified Kubelka–Munk model two green glazes (Table 1) were prepared with the same procedure using yellow zircon–praseodymium and blue zircon–vanadium pigments in the ration 65/35 and 70/30 respectively. The values of reflectance of these two green glazes were measured experimentally and confronted with that predicted by the simplified Kubelka–Munk model.

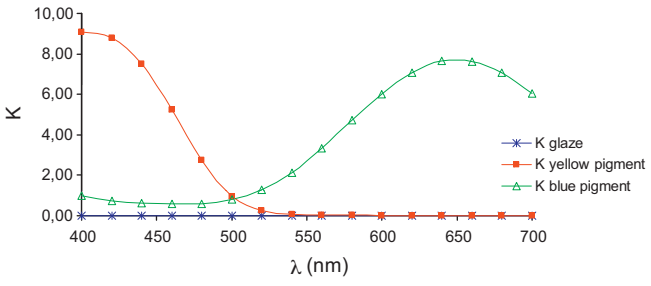

Fig. 6. Absorption coefficients of the Kubelka–Munk simplified model.

4. Results and discussion

Fig. 1 shows the morphology of the yellow and blue zircon pigments used. The yellow zircon–praseodymium pigment

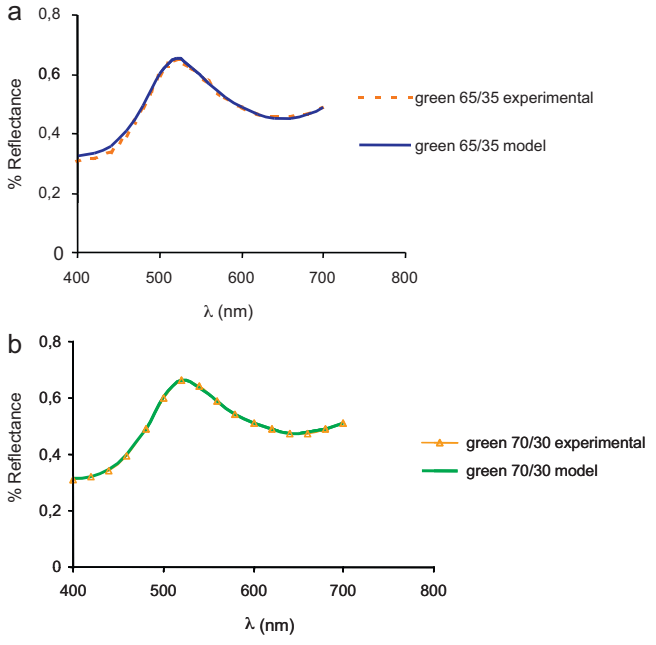

Fig. 7. Reflectance curves predicted by simplified Kubelka–Munk model for the green glazes in comparison with the experimental data. (a) Green glaze 65/35; (b) green glaze 70/30.

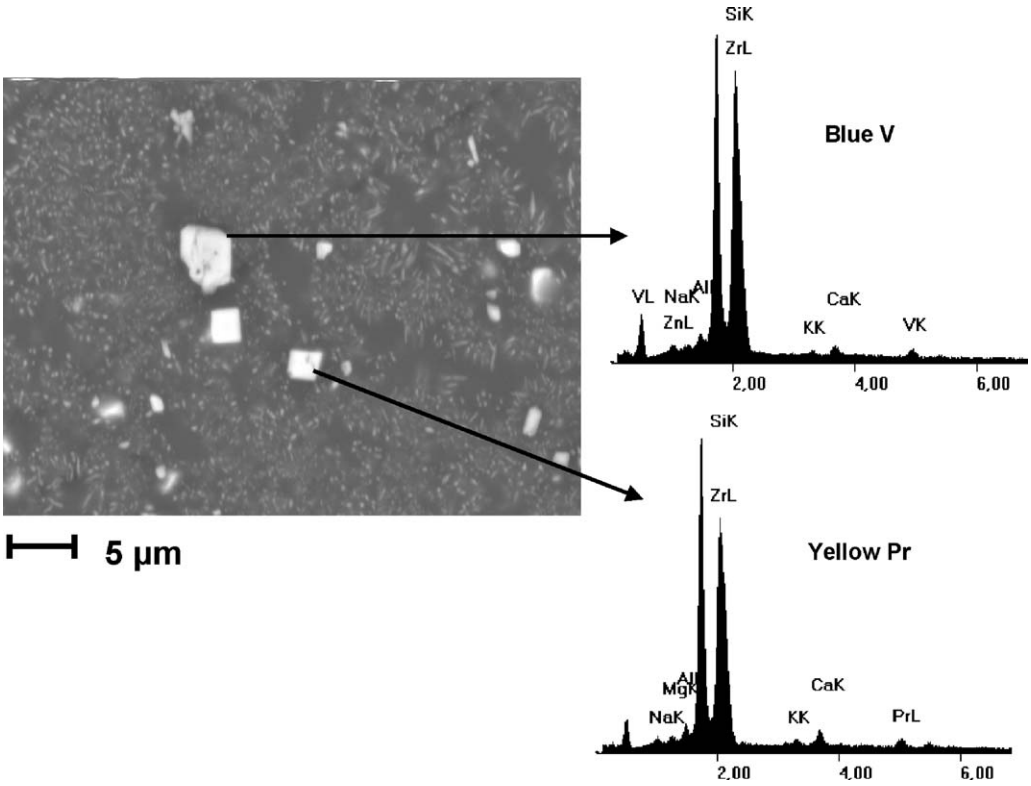

Fig. 8. SEM micrograph and EDS analysis of the green glaze (65/35) after firing.

presents, as confirmed by laser granulometry (Fig. 2), a medium particle size of 3 μm, whereas the blue zircon–vanadium pigment of 9 μm, both with a monomodal grain size distribution. The XRD analysis of the two pigments confirms the presence of zircon ($ZrSiO_4$) phase with a small amount of baddeleyite (m-ZrO_2). As supposed, the SEM-EDS analysis and XRD pattern confirm that the frit used in this study devitrifies zircon crystals (Fig. 3) responsible of the opaque proprieties of the obtained glazes. The amount, size and shape of *in situ* crystallized zircon during the firing step can change as the sintering temperature is changed. A precursor study demonstrated[12] that at 1175 °C this glaze devitrified zircon crystals with a particle size ranging from 0.60 to 0.75 μm assuring a high light scattering. Moreover these particles, due to the high reactivity of vitreous phase, show a spherical shape that also contributes to the high light reflectance.

Fig. 4 shows the glazes produced after firing. The CIELab parameters of these samples are presented in Table 1. As can be seen, the white glaze presents high lightness value (L^*), typical of opaque glazes, while the L^*, a^*, b^* values for the other samples are characteristics of the developed colours. In Fig. 5 the reflectance curves of the three samples prepared for the determination of Kubelka–Munk constants are showed. The glaze presents high reflectance values (around 0.90%) practically constant in the wavelength of visible region, as characteristic for white glazes. As expected the yellow glaze has a significant reflectance in the region from 560 to 700 nm, while the blue glaze show it in the region from 400 to 480 nm.

Using Eq. (1) from these reflectance curves of the three prepared glazes (glaze, yellow glaze and blue glaze), the K/S values were calculated at each wavelength of visible region and the obtained curves were utilized to determine the Kubelka–Munk constants, using Eq. (6) as described in Section 2 (Fig. 6). The obtained values, inserted in Eq. (7), allowed the glaze colour prediction for every blue and yellow pigments concentrations. Because the yellow zircon pigment produce main absorption at wavelength minor than 500 nm and the blue zircon pigment at wavelength higher than 560 nm, the mixture of these pigments (subtractive mixture) produces a reflectance band between 500 and 560 nm, characteristic of green colour.

To verify the suggested model, two target green colour (reported in Table 1) were reproduced. The predicted reflectance curves are showed in Fig. 7 in comparison with the experimental data. An excellent agreement between the experimental and the calculated curves was observed with deviations lower than 1.0%. In particular, Fig. 8 shows the microstructure of the green glaze (65/35) after firing. SEM and EDS analysis evidence a good dispersion of the blue and yellow zircon pigments in the glaze, confirming that these zircon pigments are stable at the used firing temperature.

5. Conclusions

The obtained results show that using the suggested simplified Kubelka–Munk model was possible to predict the colour of green glazes obtained by blue and yellow pigment mixture with good accuracy. Moreover it is important to note that with the

adopted procedure only three samples (white, blue and yellow) have to be prepared and is not necessary to prepare any samples with yellow and blue mixture to predict the colour of green glazes. This simple technique permits to determine the required quantities of yellow and blue zircon pigments to obtain a desired green colour, facilitating the formulation step.

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