METHOD FOR COLOUR ADJUSTMENT IN COLOURED OPAQUE GLAZES (I)

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1. ABSTRACT

Controlling and adjusting shades in coloured glazes is one of the main problems involved in manufacturing this kind of products. The colour adjustment method has allowed a high degree of automation to be achieved in preparing coloured glazes.

In general, coloured systems starting with an opacifier and three colorants have shown good agreement with colorimetric theories. The theory is based on glaze colour measurement with each colorant and as well as in combination with the opacifier. The advantage of this method is the reduction in the number of samples required for the adjustment. Using this theory, a computer programme has been developed which allows computing the colorants needed to obtain a given colour.

2. INTRODUCTION

Controlling and adjusting colour is currently of considerable importance owing to ever stricter quality requirements. On the other hand, fast single-firing cycles raise the sensitivity of glazes to colour changes. It has therefore become necessary to accurately characterize and control coloured glazes.

2.1 COLOUR CHARACTERIZATION AND DIFFERENCE FROM THE REFLECTANCE CURVE

The colour of an object depends on the energy distribution per incident wavelength and the light fraction that it reflects per wavelength. By plotting reflectance versus wavelength, the reflectance curves are obtained, which characterize a colour.

However, the human observer can only distinguish three stimuli called primary colours. Combining these primary colours allows the perception to be equalled, which is caused by light of a certain wavelength. In other words, light of a certain wavelength contributes to a specific extent to each of the three visually perceivable primary stimuli. A series of mathematical transformations enables making a reflectance curve correspond to three parameters or chromatic coordinates, which characterize a colour as perceived by the human observer.

This is mathematically expressed by formulas (1a) to (1c), where E_λ represents the energy distribution of the illuminant, X_λ, Y_λ, Z_λ are the tristimulus curves (the influence of each wavelength on the three stimuli) and R_λ the reflectance of the object, always in function of wavelength (λ). The energy distribution curves for each illuminant and those of the tristimuli can be found in the literature (1). The chromatic coordinates X, Y, Z can thus be calculated:

$$X=100\frac{\int E_\lambda \bar{x}_\lambda R_\lambda d\lambda}{\int E_\lambda \bar{y}_\lambda d\lambda} \qquad \textbf{(1a)}$$

$$X=100\frac{\int E_\lambda \bar{y}_\lambda R_\lambda d\lambda}{\int E_\lambda \bar{y}_\lambda d\lambda} \qquad \textbf{(1b)}$$

$$X=100\frac{\int E_\lambda \bar{z}_\lambda R_\lambda d\lambda}{\int E_\lambda \bar{y}_\lambda d\lambda} \qquad \textbf{(1c)}$$

where, by definition, for a perfect white Y = 100. There are different colour scales, by means of which it is intended, by varying their parameters to achieve corresponding variations in the observer's visual perception, that is, obtain uniform scales.

One of the most widespread systems is the CIELAB system. According to the CIELAB system, a colour is defined by three parameters: lightness (L*), redness-greenness (a*) and yellowness-blueness (b*). Figure 1 shows the definition of a colour using these three variables.

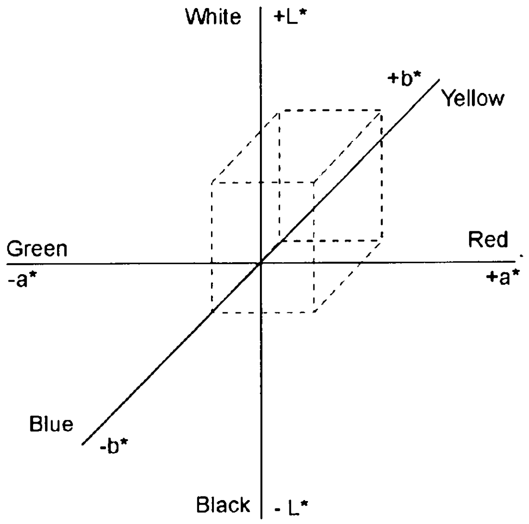

Figure 1. Chromatic coordinates of a colour.

The CIELAB coordinates are obtained from parameters X, Y, Z and reference white values X_n, Y_n, Z_n, also to be found in the literature (1):

$$L*=116(\frac{y}{y_n})^{1/3}-16 \tag{2a}$$

$$a*=500[(\frac{x}{x_n})^{1/3}-(\frac{y}{y_n})^{1/3}] \tag{2b}$$

$$a*=200[(\frac{y}{y_n})^{1/3}-(\frac{z}{z_n})^{1/3}] \tag{2c}$$

From these parameters, the difference between two colours, defined as ΔE, is given by the equation:

$$\Delta E=\sqrt{(\Delta L*)^2+(\Delta a*)^2+(\Delta b*)^2} \tag{3}$$

where:

$$\Delta L*=L*-L*' \tag{4a}$$

$$\Delta a*=a*-a*' \tag{4b}$$

$$\Delta b*=b*-b*' \tag{4c}$$

Generally, in ceramic products, a value of ΔE of less than 1 is considered acceptable, although this value depends on the use to which the product is to be put.

2.2 KUBELKA-MUNK THEORY

An approach that correlates the reflectance values of a glaze with those obtained for the same glaze by using only individual colorants, is the Kubelka-Munk theory. According to this theory, the values of the coefficient of absorption (K) and diffusion (S) of a glaze ($_s$) at a given wavelength can be calculated from the following equations:

$$K_s=\Sigma_i c_i K_i+c_b K_b \tag{5}$$

$$S_s=\Sigma_i c_i S_i+c_b S_b \tag{6}$$

where c_i are the colorant concentrations in the glaze, and c_b the opacifier concentration. Their values of (K/S) can be computed from the reflectance curve of a glaze, using the ratio:

$$\frac{K}{S}=\frac{0,45(1-R)^2}{(R^2+1,36R-0,056)} \tag{7}$$

The coefficients of this equation are empirical, and valid for ceramic surfaces (2).

These three equations allow the values of K_i and S_i to be directly calculated from the measured reflectance (R) values. Therefore, formulating glazes in which the opacifier is replaced by a colorant (pigment), and preparing a composition between the glaze with each pure colorant and the glaze with the opacifier, the values of (K/S) can be calculated from Equation (7) of the glazes of: each pure pigment ($_p$), the compositions ($_c$) and the opacifier ($_b$); and c from Equations (5) and (6):

$$\left(\frac{K}{S}\right)_c=\frac{c_pK_p+c_bK_b}{c_pS_p+c_bS_b} \tag{8}$$

Assuming that the opacifier is a perfect light diffuser, then $S_b = 1$, $K_b = (K/S)_b$ so that:

$$S_p=\left(\frac{c_h}{c_p}\right)\frac{(K/S)_c-(K/S)_h}{(K/S)_p-(K/S)_c} \tag{9}$$

$$K_p=\left(\frac{K}{S}\right)_pS_p \tag{10}$$

The values of (K/S) of the compositions of these colorants with the opacifier can be calculated from the values of K_p and S_p obtained for each colorant; and from these, the reflectance curve (Equation (7)), and the coordinates L*, a* b* can be derived. It must be taken into account that as substituting the opacifier by one or more pigments is involved, the sum of the opacifier and colorant concentrations must always be constant. This value (C) will be termed total concentration. Using this value, the specific concentrations of each colorant can be defined (x_i):

$$\Sigma_i c_i+c_b=C \tag{11}$$

$$x_i=\frac{c_i}{C} \tag{12}$$

$$\Sigma_i x_i+x_b=1 \tag{13}$$

Given the reflectance curve of a sample to be matched, the values of $(K/S)_s$ of the colour can be computed, obeying:

$$\left(\frac{K}{S}\right)_s=\frac{\Sigma_i x_iK_i+(1-\Sigma_i x_i)(K/S)_b}{\Sigma_i x_iS_i+(1-\Sigma_i x_i)} \tag{14}$$

This must be valid for each wavelength between 400 and 700 nm. Using this series of equations, it is possible to calculate the values of the colorants to be used (x_i).

As a colour is defined in the CIELAB colour space by the three coordinates L*, a*, b*, using three colorants we can attempt to cover a sector of this space whose size will depend on how linearly independent the vectors are which define these colorants. It will be possible to obtain any colour lying within this sector of the space by linearly combining these three colours and the opacifier.

There are three unknown values to be determined on basing ourselves on a system with three colorants, so that three equations will be required of the Equation (14) series, in order to obtain a system of equations allowing calculation of the concentration values of each colorant x_i. From a first valid point, the solution can be improved if the value of ΔE between the colour to be adjusted and the value calculated by this equation, is minimized. Thus, the concentrations of each colorant can be calculated from a reflectance curve.

2.3 ELABORATION OF A PROGRAMME TO IMPROVE THE COLOUR CALCULATION

Using the Kubelka-Munk equations some concentrations are obtained for the calculated colour. When a sample is prepared with these concentrations, a glaze is obtained which, according to each case in turn, approaches the colour sought to a greater or lesser extent. In general, the less opaque the glass is, or the less some of its components are colour saturated, the greater the deviation in values is. The particle-size distribution of the colorants has an effect on this (2). If the error was due to lack of opacification, it could not be assumed that $S_b = 1$, so that the measured value ($_m$) must correspond to:

$$(\frac{K}{S})_m = \frac{\Sigma_i x_i K_i + (1 - \Sigma_i x_i)(K/S)_b S_b}{\Sigma_i x_i S_i + (1 - \Sigma_i x_i) S_b} \tag{15}$$

At this point it was decided to resort to recalculating the values of the coefficient of diffusion for white (S_b) from solved Equation (15), as on the basis of the value of the measured colour $(K/S)_m$ a new parameter can be included:

$$S_b = \frac{\Sigma_i x_i K_i - (K/S)_m \Sigma_i x_i S_i}{(1 - \Sigma_i x_i)[(K/S)_m - (K/S)_b]} \tag{16}$$

with which the corrected coefficients of x'_i can be recalculated for the sought colour of:

$$(\frac{K}{S})_s = \frac{\Sigma_i x'_i K_i + (1 - \Sigma_i x'_i)(K/S)_b S_b}{\Sigma_i x'_i S_i + (1 - \Sigma_i x'_i) S_i} \tag{17}$$

By means of this recalculation, highly improved values were obtained with regard to the directly calculated ones. The flow diagram that corresponds to this process is shown in Figure 2.

It shows how, from the test pieces that had been prepared with the opacified glaze, the glaze with colorants and their mixes, the values of the coefficients of absorption (K_i) and diffusion (S_i) of the colorants (for each wavelength) are obtained. With these values of K_i and S_i and trying values for the colorant concentrations (x_i) it is possible to calculate the reflectance values (R), and thus the chromatic coordinates L*, a*, b* (according to the theoretical explanation set out above). These can be compared to the ones obtained by direct measurement with the colorimeter, and it is possible to compute the theoretical ΔE between both. An iterative programme allows the values of x_i to be optimized, which minimize ΔE (calculated). Up to this point it would be a direct calculation from the Kubelka-Munk theory in the literature (2), which would give us some quantities of colorant x_i with which a test piece of the calculated colour would be prepared, and the real value of ΔE obtained would be measured.

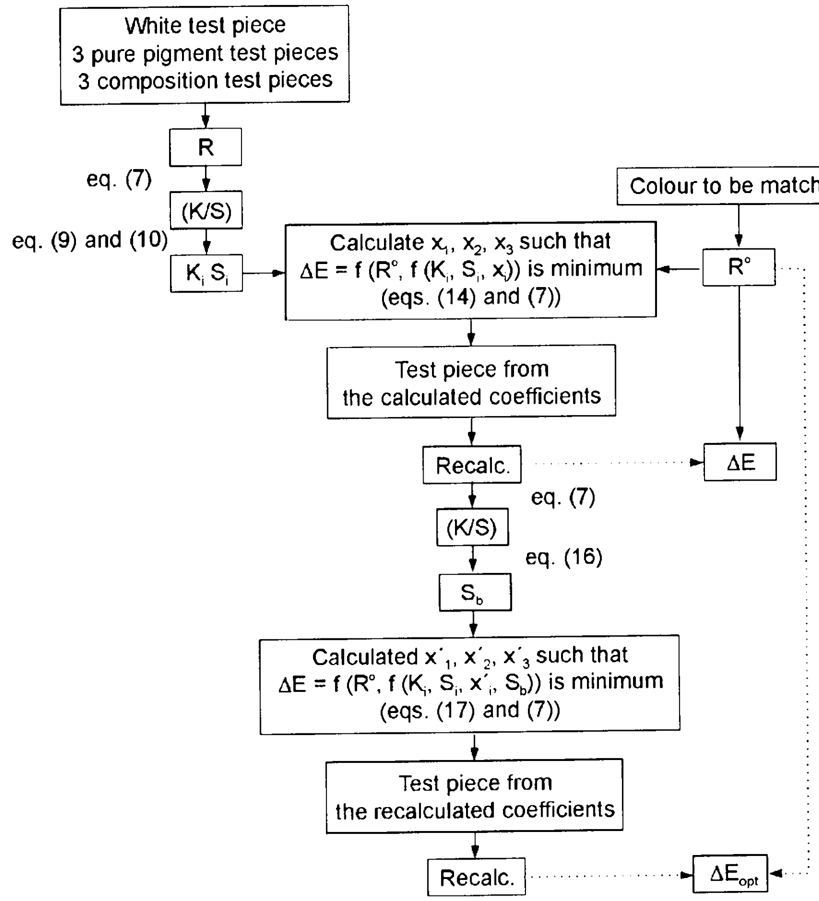

Figure 2. *Flow diagram of a colour calculation.*

Applying our correction, substituting the values of x_i obtained and the values of (K/S) calculated from the measurement performed on the colour test piece calculated in Equation (16), enables the values of S_b for the white glaze to be calculated, which will differ all the more from 1 according to how much greater the real error of ΔE has been (this is a result of having calculated the colour on the assumption that S_b was equal to 1).

With the available values of S_b, we can use Equation (17) to repeat the process of optimizing theoretical ΔE to compute new parameters (x'_i). On obtaining these new coefficients, a new test piece can be prepared whose value of real ΔE will clearly be smaller than by direct calculation.

2.4. DETERMINATION OF GLAZE TRANSPARENCY

In order to determine the transparency of the frit and glazes tested, in a solely comparative way, a transparency index (τ) was defined based on the "contrast ratio" method (1) as:

$$\tau = \frac{L*_b - L*_n}{L*_{ob} - L*_{on}} \qquad \textbf{(18)}$$

where $L*_b$, $L*_n$ are the luminosity values for each glaze, respectively on white and black backgrounds respectively (to produce a luminosity contrast), and $L*_{ob}$, $L*_{on}$ are the luminosity values of the black and white contrast backgrounds themselves.

3. OBJECTIVE

Our approach is based on adapting the Kubelka-Munk theory on opacified glazes to real situations in which we have glazes that are not 100 % opacified. The following procedure was adopted:

1. Applying this theory and determining the scope of its validity, by comparing the real values measured with a colorimeter and those calculated theoretically.
2. Preparing a programme, which by means of corrections, as set out above, allowed calculating the colours to be improved, by automating the calculation process.
3. Verifying the use of this programme in calculating two real colours.

4. MATERIALS AND EXPERIMENTAL PROCEDURE

4.1. DETERMINATION OF THE COLORIMETRIC PROPERTIES OF THE FIRED PIECES

The colorimetric measurements were performed in an ACS model CS-3 colorimeter, using the D65 light source and observer at 2°. The CIELAB (L*, a*, b*) chromatic coordinates were calculated from the reflectance curves obtained, either by using the colorimeter software, or from the tables in the literature (1), for the computation of theoretical points.

4.2. MATERIALS

To perform this work, a porous single-fire crystalline frit (F-A) with a high degree of transparency, zirconium silicate of 5 μm as an opacifier, and a varied group of colorants were used (Table I):

Table I.

Colorant	System
Green	Cr - Si - Al
Turquoise	Zr - Si - V
Yellow	Zr - Si - Pr
Brown	Zr - Cr - Fe - Al
Coral	Zr - Si - Fe
Pink	Sn - Ca - Si - Cr

4.3 PREPARATION OF THE TEST PIECES

Glaze compositions were prepared as detailed in Table II,

Table II.

	Glaze A	Glaze B
Single-fire crystalline frit	72	82
Kaolin	8	8
Opacifier/Pigment	20	10

and these were applied onto a white single-fire clay body according to the scheme in Table III:

Table III.

1. White and black engobes applied by split skid with a liquid layer thickness of 0.026 cm at d=1.65 g/cm^3.
2. Glaze to be tested applied by skid with a thickness of 0.082 cm at d=1.65 g/cm^3.

The test pieces were fired in a laboratory muffle kiln with a cycle of the porous single-fire kind of 1100°C.

4.4 DETERMINATION OF THE TRNSPARENCY OF THE FRIT AND GLAZES USED

This took place as described in Section 2.4 using compositions with frit F-A and increasing amounts of zircon, in which the glazes with 20% and 10% zircon coincide with those defined in Table I as A and B. By applying the glazes according to the scheme in Table III, so that the white and black engobes heighten the effect of the of the contrasting backgrounds, the values in Table IV are obtained:

Table IV.

% Zircon 5μm	τ
0	0.970
2	0.831
4	0.521
6	0.440
8	0.367
10	0.299
12	0.228
14	0.224
16	0.176
18	0.179
20	0.133

These data were used to construct the graph in Figure 4, which shows that: Frit F-A with which the glazes were formulated, has a high degree of transparency (for an ideal transparent glaze, τ is equal to 1). None of the glazes with which work was carried out, formulated from frit F-A, can be considered a pure opaque glaze. In a pure opaque glaze the background colour would not have any effect, and it would therefore have a value of τ equal to zero.

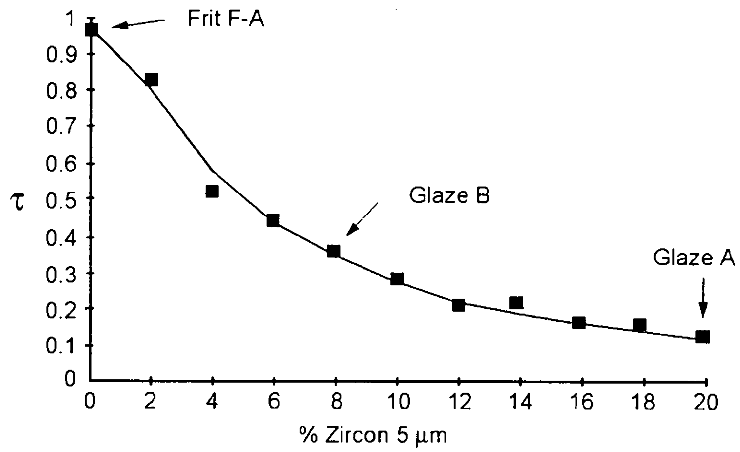

Figure 4. Frit and glaze transparency.

4.5. APPLICATION OF THE KUBELKA-MUNK THEORY TO COLOUR CALCULATION

4.5.1.Calculation of coefficients K_i and S_i of the colorants

Glazes were prepared according to the formulations in Table II, where the opacifier is Zircon 5 μm and the pigments the ones indicated in Table I. These were used to prepare mixes in the proportion 1:1 between the opacifier and the pigment, the sum of both remaining constant (C = 20). The values of K_i and S_i are obtained for the colorants from the colorimetric determination of these 7 samples (3 with pure colorant, 3 compositions, and white), by applying Equations (7), (8) and (9).

4.5.2 Determination of the scope of validity of Equation (14) for the colour calculation

As an example, glazes were prepared with compositions type A and B, and colorants substituting zircon, referenced as A_1 and B_1 in Table V:

Table V.

Raw materials	A_1	B_1
Frit A	72	82
Kaolin	8	8
Zircon 5μm	14	4
Turquoise	2	2
Brown	2	2
Coral	2	2

and these were applied, measuring their colour. On the other hand, colour was calculated in Equation (14) from the previously obtained values of K_i and S_i, in order to compare results. Calculating the colorimetric coordinates and differences between these two colours (Table VI):

Table VI.

	τ	ΔE	ΔL*	Δa*	Δb*
A_1	0.133	2.77	0.30	-0.17	2.75
B_1	0.299	10.58	-10.41	0.25	-1.89

The plot in Figure 5 shows the reflectance curves corresponding to the real colour (measured by colorimeter) and the calculated colour. The graph shows that the differences between the measured reflectances and the calculated ones are small for glaze A_1 while they increase spectacularly for glaze B_1, which is considerably less opaque. The error grows owing to the lack of opacity of the glaze (influence of the engobe colour). On increasing the glaze layer and/or opacity, the effect of the background is less and the result improves (this was substantiated in a series of experiments performed by varying the thickness of the skid used).

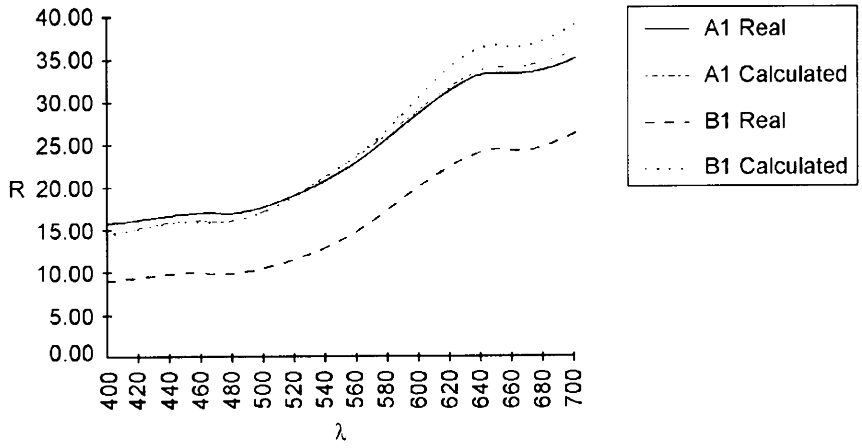

Figure 5. Real versus calculated colours.

4.6 VERIFICATION OF THE PROGRAMME FOR COLOUR MATCHING BY RECALCULATION

Two of the colour calculations performed are given as an example. The first was expressly designed to check in what way the programme is capable of adjusting the colorant coefficients. The second is an actual case of adjustment using a colour with an unknown composition.

4.6.1. Matching a colour of the same glaze

A colour to be matched was prepared with formulation C in Table VII:

The colour was measured with the colorimeter and the programme was adjusted, obtaining the three coefficients of the colorants to be used (C_1 in Table VII). A test piece was prepared with this formulation and its colour was measured. The result was used to correct the colour, obtaining the new corrected coefficients (Formulation C_2). This formulation was also employed to prepare a test piece, whose colour was determined in the colorimeter. The colour differences obtained for glazes (C_1, C_2) in Table VII in relation to reference (C) are shown in Table VIII:

Table VII.

Raw materials	C	C_1	C_2
Frit A	72	72	72
Kaolin	8	8	8
Zircon 5μm	14.54	13.75	14.39
Turquoise	1.82	2.42	1.84
Yellow	1.82	2.21	1.95
Pink	1.82	1.62	1.82

Table VIII.

	ΔE	ΔL^*	Δa^*	Δb^*
C_1	3.28	-0.47	-3.15	0.79
C_2	0.64	-0.04	-0.18	0.61

Table VIII shows that much better results are obtained with the correction than were obtained with Equation (14), and that ΔE decreases to almost tolerable values. It can be observed in Table VII that the recalculated coefficients highly resemble the initial ones. Only yellow deviates appreciably. This is because the values of the coefficient of absorption (K) for yellow from 540 nm on are very low, and are obtained with a greater error than for the rest of the colorants. However, this variation in the coefficient does not significantly influence the colour, with ΔE remaining smaller than 1.

4.6.2. Matching a colour from its reflectance curve

The graph in Figure 6 was obtained from the colour measurement of a glaze with an unknown composition (referenced "problem"), plotting reflectance versus wavelength. This graph shows that the problem colour is a shade of green, by the reflectance peak in the intermediate domain of the spectrum between 500 and 580 nm. Three colorants were used to match this colour: green as main shade, and turquoise and pink to correct the curve at the ends (turquoise reflects low λ values and pink high ones).

By introducing the reflectance values of the sample into the programme, together with the values of K_i and S_i of the colorants in a formulation of the glaze A type in Table I, the direct coefficients (D_1) are obtained. On performing a recalculation like the one developed above, glaze D_2 is found.

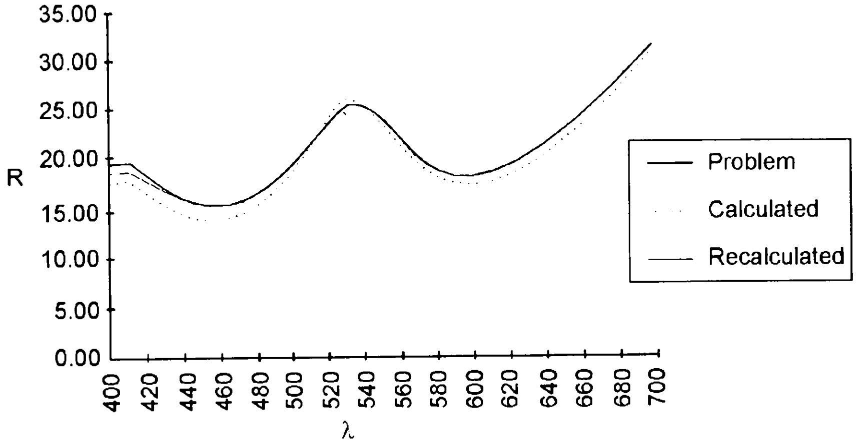

Figure 6. Matching the glaze D colour.

Table IX.

Raw materials	D_1	D_2
Frit A	72	72
Kaolin	8	8
Zircon 5μm	15.05	14.69
Green	2.68	2.08
Turquoise	1.27	1.75
Pink	1.00	1.48

The colour differences for these glazes (D_1 calculated and D_2 recalculated) are shown in Table X, and their reflectance curves together with that of the reference are found in Figure 6. This figure shows that the reflectance values for the colour to be matched and the recalculated ones virtually coincide from 450 nm on, while the ones calculated by the direct method still differ considerably. The value of ΔE obtained by recalculation is much smaller than the one obtained directly.

Table X.

	ΔE	ΔL*	Δa*	Δb*
D_1	3.25	-0.94	-2.27	2.12
D_2	1.01	-0.11	-0.82	0.58

5. CONCLUSIONS

The Kubelka-Munk theory has been shown suitable for calculating colours, as long as a sufficiently opaque glaze is involved. When this is not the case, as often occurs in commercial glazes, the theory gives rise to problems of agreement.

However, it has also been shown that by incorporating a recalculation, the results obtained directly can be corrected, achieving much closer fit. By applying a computer to this system, colour matching becomes easy and fast, as few test pieces need to be prepared. This is of major interest in wall tiles, whether manufactured by porous single firing or fast twice firing, since a small number of glazes are involved and after having calculated the coefficients K_i and S_i for a group of colorants, obtaining a new colour is brought back to performing two tests.

Applying this programme allows the composition of colorants to be easily simulated, which is applicable to the obtainment of stable, commercial colours. On giving values to the coefficients of the colorants, it can be observed how the corresponding reflectance curves vary, and how a percent change in a colorant would affect the calculated theoretical ΔE.

It is possible to go even further, as readapting the programme enables a fast readjustment of colours that may have deviated from a set reference. Especially when the reference colour has been formulated according to this calculation programme, the readjustment can be performed with the same colorants. Moreover, if colorants are available that can be prepared by mixing with a ground base without colorants (with the advantages that this method entails), the system becomes quite mechanized.

There is also a series of advantages in this method of readjustment compared to classical linear interpolation (based on colour measurement in incrementally modified glazes and the calculation of the obtained colour differentials), which would be:

- Reduction in the number of samples, as the preliminary test pieces are prepared for individual colorants and are applicable to all the colours that can be prepared with the same type of base, while linear readjustment requires preparing test pieces with compositions close to that of the reference, slightly varying the amounts of colorant involved.

- Amplification of the range of adjustment, because on being based on equations that approximate the colour calculation, quite reliable data can be extrapolated, while in linear fitting only interpolation is possible.

6. REFERENCES

(1) Hunter, Richard S., Harold, Richard W. "The Measurement of Appearance" (2ª ed.) (1987).

(2) Murdock, Stephen H., Wise, Terry D. "Predicting the Color of a Ceramic Glaze" Ceramic Bulletin, vol 69, nº 2, (1990).