APPLICATION OF GONIOSPECTROPHOTOMETRY TO THE CHARACTERISATION OF SPECIAL DECORATIVE EFFECTS

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ABSTRACT

The evaluation of the colour of so-called 'metallised' glazes is an important problem, especially since there is no clear definition for this type of material. The study shows that a spectrophotometer is not sufficient for evaluating the colour of these glazes, whereas a goniospectrophotometer with four angles of viewing enables a set of data to be obtained that more closely describe glaze appearance. However, the description of the colour component of glaze appearance using twelve chromatic coordinates is difficult to handle. For that reason, an index is proposed, similar to the whiteness or yellowness indices, for the evaluation of 'metallised' appearance. This index is calculated from the goniospectrophotometer data, and has allowed 'metallised' glazes to be differentiated from 'non-metallised' glazes, in the set of samples used in this study.

1. INTRODUCTION

Colour measurement is a common operation in many sectors, both in laboratories and on an industrial scale, using tristimulus colorimeters or spectrophotometers. In the ceramic field, instrumental colour measurement of uniform tile colour is quite a widespread technique. Indeed, there are standards on the measurement of tile colour, as well as of colour differences, aimed at detecting deviations in relation to a production standard [1]. Despite the progress in instrumentation, however, it is ultimately the human observer who will assess whether two samples have the same appearance or not, and that leads to notable problems when it comes to evaluating tiles that display specific difficulties.

In recent years, the spread of the use of so-called 'metallised' glazes, whose optical properties resemble those of old lustres, has posed a notable challenge to colorimetric techniques since these glazes have a very special characteristic: their colour changes as a function of the angles of illumination and of observation, making it very difficult, visually or instrumentally, to determine whether two samples have the same appearance. In fact, there is not even a widely accepted definition of what a 'metallised' appearance involves, though some attempts have been made to define its characteristics from an optical standpoint [2].

In other sectors, such as the automotive sector, colorimetric measurements for this type of material are made with goniospectrophotometers, these being instruments that are able to measure colour from different angles of observation, at an illumination with a given angle of incidence [3]. In principle, the measurements should be made for any combination of angles of incidence and of observation, in order to obtain a full description of glaze appearance, but in many standards, it is considered sufficient to perform the measurements at a fixed angle of illumination, and to obtain the chromatic coordinates at four judiciously chosen angles of observation. The chromatic coordinates enable the colour difference ΔE for each angle of observation to be evaluated and defines the allowable maximum difference, according to the working conditions [4].

Although the chromatic coordinates or colour differences can be determined as a function of the angle of observation, no single parameter has been defined that can be considered to evaluate the 'metallised' appearance of a glaze. This study puts forward a preliminary proposal of a 'metallic appearance index', based on colour measurements at four different angles and on a simplification of the CIELab colour space. The proposed index has been experimentally validated with a group of glazes of different characteristics.

2. EXPERIMENTAL

This study has been performed on 27 different glazes. Twenty of these were glazes of different colours with a 'metallised' appearance. The other glazes had a 'non-metallised' appearance, and were produced from mixtures of frit and pigments in different proportions.

Glaze colour was evaluated using two different instruments:

- A spectrophotometer with an integrating sphere with diffuse/8º geometry, which analyses all the light reflected by the sample (Macbeth Color-Eye 7000A).
- A goniospectrophotometer according to standard DIN 6175-2 [4], whose optical configuration allows, at a 45º angle of illumination, the spectral composition of the light returned by the sample at 4 aspecular angles of observation: 25º, 45º, 75º, and 110º to be determined, the aspecular angle being defined in relation to the direction specular to the illumination (Macbeth 740GL).

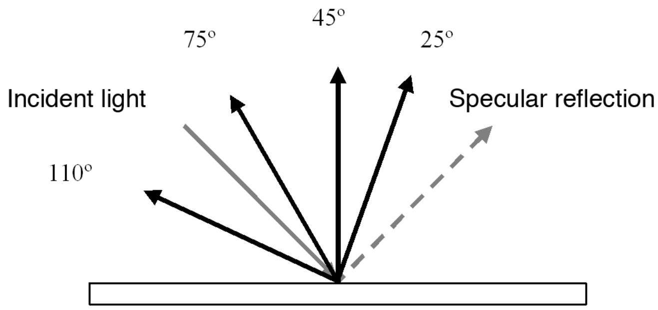

Figure 1. Schematic illustration of the incident angles (45º in relation to the normal) and measurement angles (25º, 45º, 75º, and 110º in relation to the specular reflection) of the goniospectrophotometer used.

Five measurements were made per sample with both instruments, using a CIE standard illuminant D_{65} and CIE 10º standard observer, obtaining the reflectance curves as a function of the wavelength for each angle, using the reflectance curves to obtain the CIELab chromatic coordinates [5].

3. RESULTS

3.1. Comparison of the two colour measurement instruments.

Both instruments were used to determine the chromatic coordinates of the 27 glazes and thus to compare the resulting data (table 1 and table 2). The tables show clearly that the chromatic coordinates obtained with the spectrophotometer differ notably from those generated by the goniospectrophotometer in most cases, which is consistent with the different mode of operation of each instrument (collection of all the radiation returned from the surface versus collection of the radiation fraction returned in specific directions). In the goniospectrophotometer data, however, it may be observed that the chromatic coordinates obtained at each angle vary quite markedly in the 'metallised' glazes, whereas the variations are very small in the samples that did not display this property. This fact corresponds to the characteristic of metals to return the greatest proportion of light in the specular direction, and to return a smaller proportion of light as the measurement angle moves further away from that direction.

The differences in the values of the chromatic coordinates obtained at each angle are the result of notable changes in the reflectance curves. By way of example, figures 2 and 3 depict the reflectance curves obtained for samples A03 and A19. In glaze A03, it may be observed that the glaze displays maximum reflectance at all wavelengths for the angle closest to the specular direction (25º) and, as the angle of observation increases, reflectance decreases, though not progressively but in a very pronounced fashion at the beginning (45º) and very slightly at the end (75º and 110º). In glaze A19, the behaviour is qualitatively similar but much less pronounced, since the shift of the reflectance curves versus the measurement angle is much smaller. It may further be observed that the curves do not shift uniformly, but that curve shape can change completely, as occurs in A03.

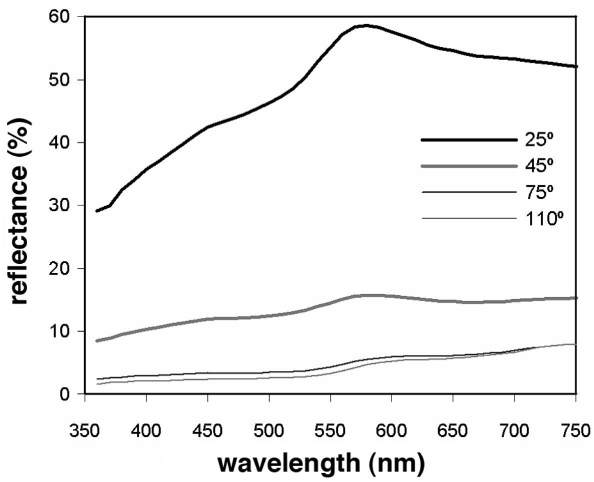

Figure 2. Evolution of reflectance versus wavelength and measurement angle for glaze A03.

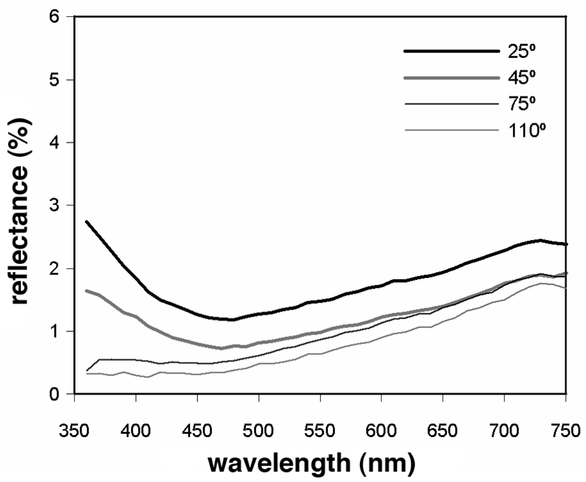

Figure 3. Evolution of reflectance versus wavelength and measurement angle for glaze A19.

Glaze	spectrophotometer			goniospectrophotometer			
	L*	a*	b*	angle	L*	a*	b*
A01	68.4	-2.2	5.2	25º 45º 75º 110º	36.4 15.1 9.5 9.0	0.5 3.6 5.5 5.9	3.8 5.9 7.0 7.2
A02	57.6	10.3	8.8	25º 45º 75º 110º	75.6 52.6 35.8 35.0	9.3 10.6 13.5 13.2	9.3 8.1 8.4 7.7

A03	57.2	2.0	9.9	25º 45º 75º 110º	78.0 44.5 25.5 22.7	1.3 1.7 5.9 7.8	12.1 6.2 7.4 9.4
A04	60.5	2.0	5.0	25º 45º 75º 110º	29.0 23.0 22.1 21.3	12.4 17.3 19.4 20.4	10.5 18.8 22.6 24.1
A05	60.3	-1.6	4.0	25º 45º 75º 110º	57.0 24.2 16.2 16.5	-1.5 5.6 12.1 13.4	0.1 3.0 9.6 12.2
A06	72.4	1.8	10.6	25º 45º 75º 110º	53.6 27.1 20.8 21.1	7.4 12.7 15.6 16.7	10.6 14.0 18.5 19.9
A07	70.8	5.6	13.0	25º 45º 75º 110º	48.3 28.2 20.9 19.7	13.8 16.3 18.1 19.3	15.9 17.4 19.2 20.0
A08	54.9	15.2	11.6	25º 45º 75º 110º	67.3 41.8 29.7 26.7	14.9 18.4 20.5 20.0	10.6 12.6 14.8 13.8
A09	57.5	10.1	8.2	25º 45º 75º 110º	75.0 45.1 33.2 32.6	8.2 12.8 15.6 14.3	7.8 7.8 9.0 8.0
A10	68.8	8.6	15.5	25º 45º 75º 110º	51.7 31.8 23.5 21.8	14.9 17.5 18.9 19.8	16.8 18.9 19.6 19.7
A11	59.7	15.2	14.3	25º 45º 75º 110º	58.8 37.4 27.8 25.0	17.6 19.9 21.1 20.7	14.1 16.8 18.2 17.1
A12	62.9	8.2	17.3	25º 45º 75º 110º	83.0 45.3 28.3 22.6	8.0 8.0 11.3 11.8	19.9 12.5 11.3 10.8
A13	56.8	2.8	8.5	25º 45º 75º 110º	71.9 52.7 33.6 29.6	2.9 2.8 4.4 5.8	10.4 7.7 5.6 5.8
A14	69.2	-0.9	3.0	25º 45º 75º 110º	36.1 21.4 16.9 16.3	7.0 13.0 14.4 15.1	9.1 18.4 19.5 20.2
A15	68.3	-2.2	2.1	25º 45º 75º 110º	33.9 17.8 14.1 13.8	5.8 10.2 11.2 11.7	8.8 14.7 15.2 15.9
A16	69.9	-1.1	9.5	25º 45º 75º 110º	80.3 31.8 16.1 16.4	-2.0 2.5 9.4 10.8	7.9 4.8 9.1 11.5
A17	69.7	-3.5	4.4	25º 45º 75º 110º	39.0 16.0 10.0 9.6	0.3 4.3 7.9 9.3	1.1 3.2 7.3 8.9
A18	54.4	8.6	19.4	25º 45º 75º 110º	15.2 4.4 1.8 1.2	0.9 0.1 0.5 0.0	4.2 1.6 0.8 0.4
A19	57.3	2.6	11.4	25º 45º 75º 110º	12.6 9.1 7.9 6.1	2.9 3.1 3.1 3.1	2.4 2.8 5.8 5.2
A20	56.0	6.5	24.7	25º 45º 75º 110º	13.0 4.5 3.1 2.7	0.1 -0.1 0.4 -0.8	1.8 0.4 1.1 0.2

Table 1. Chromatic coordinates of the studied 'metallised' glazes.

Glaze	spectrophotometer			goniospectrophotometer			
	L*	a*	b*	angle	L*	a*	b*
A21	64.8	1.3	4.0	25º 45º 75º 110º	62.7 62.0 61.7 61.8	1.5 1.5 1.5 1.5	4.5 4.8 4.6 4.3
A22	94.3	-0.9	0.9	25º 45º 75º 110º	94.3 94.3 94.3 94.6	-1.1 -1.1 -1.0 -1.0	1.1 1.4 1.2 1.0
A23	26.8	0.4	0.0	25º 45º 75º 110º	3.5 3.2 3.5 3.8	1.6 1.5 2.0 2.1	0.8 1.0 1.2 1.2
A24	53.8	39.9	27.8	25º 45º 75º 110º	49.7 49.3 49.2 49.5	45.5 46.0 46.0 45.7	35.2 36.1 35.9 35.5
A25	42.3	-11.2	13.8	25º 45º 75º 110º	35.0 34.5 35.1 35.9	-15.3 -15.6 -15.4 -15.6	21.7 22.0 21.5 21.6
A26	83.0	-3.7	73.5	25º 45º 75º 110º	82.3 82.0 81.7 81.7	-3.6 -3.6 -3.6 -3.6	85.8 86.4 86.2 86.0
A27	27.2	10.3	-20.3	25º 45º 75º 110º	6.1 5.6 5.1 4.9	32.2 32.2 32.3 31.0	-42.4 -42.4 -42.1 -40.8

Table 2. Chromatic coordinates of the studied 'non-metallised' glazes.

As it has already been noted, the data in table 1 correspond to the average values of five measurements, and one might ask whether the notable variations in colour detected as a function of the measurement angle correspond to local changes in the optical characteristics of the surface of the 'metallised' glazes. In order to clear up this point, the difference in colour of the five measurements performed on each glaze in relation to their average value was calculated. The equation in German standard DIN 6175-2 [4] for colour tolerances in 'metallised' paints of the automotive sector has been used for this calculation. This equation provides a closer approximation to the visual perception of the colour differences and differs from that proposed by the CIELab* system (equation 1) in regard to the weight assigned to the variation of each chromatic coordinate in the evaluation of ΔE_{DIN}. The average values of ΔE_{DIN}, calculated according to this standard for each 'metallised' glaze, have been plotted in figure 4.

$$\Delta E^* = \sqrt{(L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + (b_2^* - b_1^*)^2}$$

Equation 1.

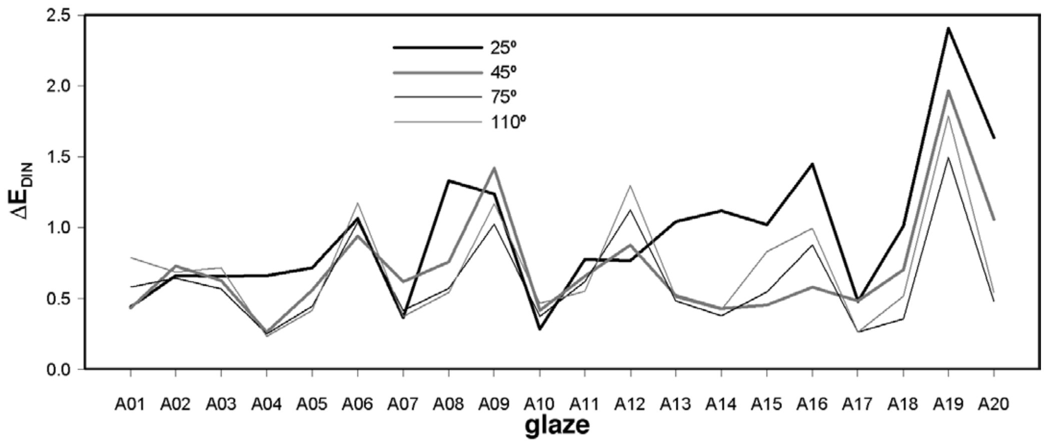

Figure 4. Colour difference ΔE_{DIN} between the different measurements with respect to the average in each 'metallised' glaze (according to standard DIN 6175-2).

It may be observed that the average colour difference obtained between the different points on the glaze surface with respect to the average value is less than 2 for all test samples and angles, except in one case. Since this standard considers that a value of ΔE_{DIN} above 1 already constitutes an appreciable visual difference, this means that some of the glazes already display visually appreciable heterogeneities in colour in the same piece, heterogeneities that would be detectable with the four angles of measurement of the goniospectrophotometer. When the values of ΔE_{DIN} calculated with the differences in the chromatic coordinates between glazes obtained at different angles (table 1) are compared, however, the latter are generally observed to be higher than the differences in colour in the same piece. As a result, these differences may be assumed not to be due to variability in the glaze surfaces, but to real differences in the spectral composition of the light returned in each direction.

The colorimetric data indicate that the 'metallised' appearance entails important variations in the chromatic coordinates as a function of the angle of observation, a situation that does not occur in the glazes lacking this effect. As a result, one might obtain a first evaluation of the difference in 'metallised' appearance between two samples by comparing the colour difference determined with the spectrophotometer with those determined as a function of the angle of observation with the goniospectrophotometer. In accordance with this assumption, figure 5 shows a plot of the colour differences ΔE^* between samples A03 and A19, obtained for the five colour evaluation conditions for each glaze (i.e. the data corresponding to the spectrophotometer and to the four angles of the goniospectrophotometer), using the CIELab* equation (equation 1). Not that the equation in standard DIN 6175-2 was not used because it is defined for small colour differences and can generate erroneous results in the case of large variations in colour, as in this case. In order to facilitate the visualisation of the differences, the points corresponding to the measurements in the CIELab colour space have also been plotted (figure 6).

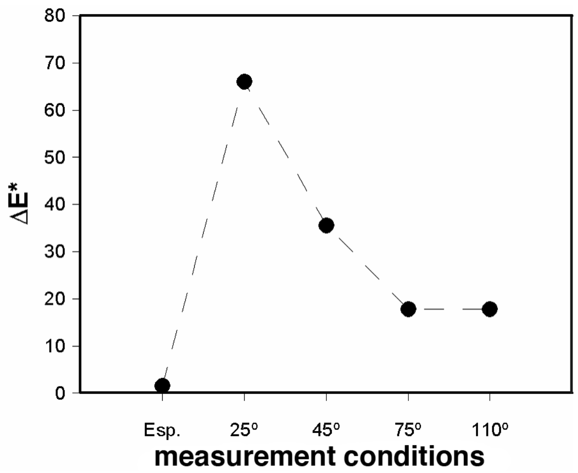

Figure 5. Colour differences ΔE* between glazes A03 and A09 as a function of the instrument used (Esp. is the spectrophotometer; the angles correspond to the goniospectrophotometer).

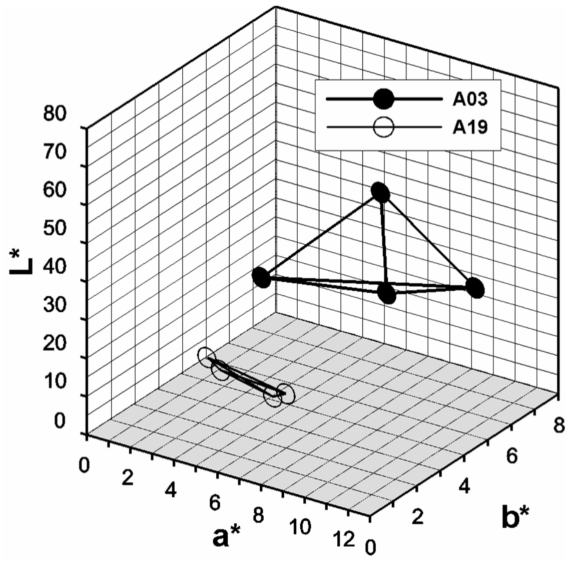

Figure 6. Situation in the CIELab space of the chromatic coordinates of glazes A03 and A19, evaluated at the four angles of the goniospectrophotometer.

Figure 5 shows that the ΔE* obtained with the spectrophotometer (Esp.) is close to unity, and much lower than that obtained for the different measurement angles with the goniospectrophotometer. Therefore, in this case, the evaluation of the colour difference with the diffuse geometry instrument could lead to the mistaken conclusion that both surfaces are very similar, when very notable differences would be visually detected, particularly when the pieces were observed at an angle close to the specular direction (25º): even at angles removed from the specular angle (75º, 110º), the visually observed difference in colour would not match that determined instrumentally. This demonstrates that spectrophotometers are inappropriate instruments for evaluating the colour of glazes with a 'metallised' appearance.

When the calculation of the colour differences performed for the pair A03–A19 is extended to all the possible combinations of 'metallised' glazes, the first outcome is that the colour difference calculated from the chromatic coordinates that the spectrophotometer provides is lower, in every case, than that obtained for the different measurement angles with the goniospectrophotometer.

By way of example, figure 7 shows a plot of the colour differences ΔE* for those pairs of samples that exhibited a value below 2 for this parameter, obtained by the spectrophotometer (Esp). It may be observed in the figure that the angle of observation at which the largest ΔE* is obtained depends on each pair of samples, while it is not the angle of 25º that leads to the greatest difference, as occurs in the pair A03–A19, but the maximum difference depends on each particular pair.

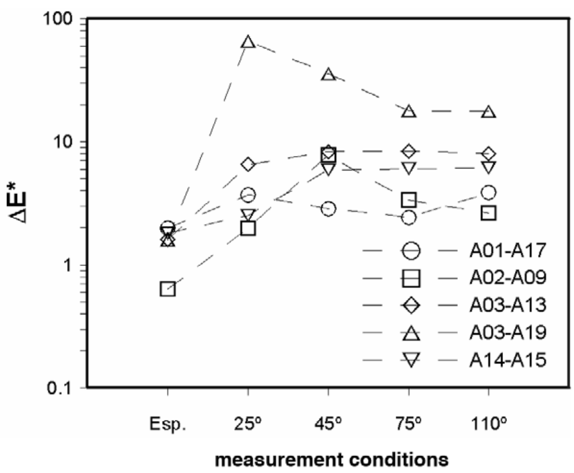

Figure 7. Colour differences ΔE for different pairs of glazes as a function of the instrument used.*

When the frequencies with which an angle of observation led to the greatest value of ΔE* in the population made up of all the possible pairs of 'metallised' glazes (see table 3) were calculated, it was found that the angle of 25º displayed the greatest frequency: this was to be expected since it was the closest to the specular direction. However, almost 30% of the pairs exhibited a maximum frequency at other angles of observation. These results indicate that the difference in the 'metallised' character of a glaze cannot be determined in terms of the ΔE* measured for the 25º angle, because there is a considerable probability that this value will not correspond to the maximum ΔE*. On the other hand, it would be desirable for the appearance of a 'metallised' glaze to be evaluated using the own colorimetric data of the glaze, without it being necessary to compare these with a particular reference.

Angle of observation	25º	45º	75º	110º
Frequency of appearance of maximm ΔE* (%)	71	18	4	7

Table 3. Frequency with which the largest ΔE was obtained for each angle of observation.*

3.2. Proposal of an index for the estimation of the 'metallised' appearance of glazed ceramic surfaces.

Given the optical properties of 'metallised' glazes and considering the need to use a goniospectrophotometer for the proper characterisation of their appearance, as highlighted above, it would be possible to characterise the chromatic features of these glazes according to the usual practice in other sectors, in which the chromatic coordinates measured at four standard angles are described. It would be advisable, however, to have a parameter that allowed the 'metallised' appearance to be estimated in an objective form, since the description by means of several sets of chromatic coordinates can lead to confusion, and it is always simpler to handle a single parameter, like the whiteness and yellowness indices, even though information is obviously lost when several variables are compressed into single variable.

The proposed index for describing 'metallised' appearance is based on figure 6. When the points defined by the four triads of chromatic coordinates (L*, a*, and b*), generated by the goniospectrophotometer in measuring a 'metallised' glaze, are joined in the CIELab colour space, an irregular tetrahedron is obtained whose edges correspond to ΔE^* between the different measurement angles. In this figure, it may be observed that the tetrahedra defined for the two samples are located in different areas of the colour space and, in particular, that they have very different dimensions, which is a key indication of the variations in colour that both surfaces display as a function of the angle of observation. As a result, the longer the length of the tetrahedron edges, the greater will the colour differences for a given glaze be when the angle of observation changes. Therefore, the sum of the six edges of the tetrahedron could provide a first approximation to an index that describes 'metallised' appearance because, if there were no differences between the CIELab coordinates obtained at different angles, the value of the index would be zero. It might be countered that the volume of the tetrahedron would also be representative of the colour differences, but if the points representing the four measurements in the CIELab space were coplanar, tetrahedron volume would be zero, while the sums of the edges would still be a value that was not zero. In fact, in figure 6 the points corresponding to glaze A19 are almost coplanar.

The maximum value of the proposed index would be given by the largest tetrahedron that could be defined in the CIELab colour space, which is a finite area. A first approach can be obtained by assuming that the CIELab colour space is a sphere with a radius equal to 50, whose centre is located at L* = 50 and a* = b* = 0. In this case, the largest tetrahedron that fits into this sphere is a regular tetrahedron whose edge is equal to $100 \cdot (2/3)^{0.5}$, the sum of the six edges therefore being equal to $600 \cdot (2/3)^{0.5}$, which would be the highest value attainable by the index (figure 8).

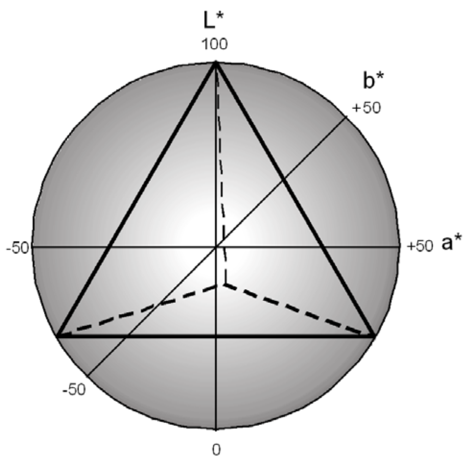

Figure 8. Schematic illustration of the largest tetrahedron that could be fitted into the simplification of the CIELab space.

In order to facilitate the understanding of the index, the value of the sum of the six edges corresponding to the colour differences of a given glaze can be normalised with respect to the maximum possible value of the sum, the final index being defined as a percentage of that maximum (equation 2). The value of I_M would thus vary between 0 and 100.

$$I_M = \frac{\Delta E^*_{25-45} + \Delta E^*_{25-75} + \Delta E^*_{25-110} + \Delta E^*_{45-75} + \Delta E^*_{45-110} + \Delta E^*_{75-110}}{600 \cdot \sqrt{2/3}} .100$$

Equation 2.

The application of this equation to the 27 test glazes yielded the results detailed in table 4. It is clear that the glazes with a 'metallised' appearance generate I_M values above 5 (A01 to A20), while the glazes lacking this characteristic (A21 to A27) exhibit index values below 2. As a result, the proposed index is able to separate 'metallised' glazes from non-metallised ones. In addition, the results indicate that the higher the value of the index, the more 'metallised' will the glaze appearance be. These findings also mean that it is necessary to use a goniospectrophotometer in order to evaluate this property, since I_M cannot be obtained from the data provided by a spectrophotometer.

Sample	I_M	Sample	I_M	Sample	I_M
A1	18.49	A10	20.37	A19	5.20
A2	28.54	A11	22.98	A20	7.01
A3	38.57	A12	41.09	A21	0.78
A4	11.65	A13	30.11	A22	0.38
A5	31.00	A14	15.74	A23	0.69
A6	23.76	A15	14.37	A24	0.82
A7	19.70	A16	44.59	A25	1.00
A8	27.76	A17	21.61	A26	0.67
A9	28.99	A18	9.46	A27	1.75

Table 4. Index for the estimation of the 'metallised' character of a glaze, calculated for all the test glazes.

The proposed index is obviously a first approximation, and further development is required in order to confirm its validity. The following tasks remain to be carried out:

- Performance of measurements on a much wide range of glazes, and correlation of the values of I_M with visual appreciations of the glazes. This would allow the range of values of I_M to be defined, above which a glaze could be considered to display a 'metallised' appearance. That study might show that the relation between I_M and visual perception is not linear, but that there might be another type of dependence which, in that case, would need to be determined.

- Recalculation of the normalisation factor, since the CIELab colour space is in reality a deformed sphere and, therefore, the problem of identifying the largest tetrahedron that could be fitted inside it is no simple matter.

4. CONCLUSIONS

Glazes with a 'metallised' appearance display colour variations depending on the angle of observation. As a result, their appearance cannot be properly evaluated with diffuse reflectance spectrophotometers since the chromatic coordinates that are evaluated with that instrument could correspond visually to colours far removed from those visually perceived. The study shows that goniospectrophotometers are more appropriate for describing the appearance of these glazes, though this entails definition of a set of chromatic coordinates for each angle of observation, which means handling a larger volume of data.

It has been verified that there is no measurement angle whose differences between two glazes can be correlated to differences in glaze 'metallised' appearance. Although measurements at an angle of 25º usually lead to the highest colour differences, this maximum can also appear at other angles of observation, depending on the glaze.

An index is proposed that allows the 'metallised' appearance of glazes to be instrumentally evaluated from the measurements of a goniospectrophotometer with four angles of viewing. The evaluation requires no external reference. Nor does it depend on the angle at which the greatest colour difference appears.

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