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Proposal of a novel formula to calculate dominant wavelength for colour of red wines*

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Dominant wavelength is a representative variable of the hue useful for the characterization of the colour of red wines. It is usually obtained through a conventional graphical method on the CIE 1931 (x,y) diagram. In this work, three alternative formulae for calculating dominant wavelength are checked on two sample groups of red and rosé wines which consist of 109 Spanish wine samples and 66 samples taken from authors in the reference list respectively. A novel polynomic quotient expression obtained by applying the 'derivative-free nonlinear regression method' is proposed for an accurate calculation of dominant wavelength.

INTRODUCTION

Among the chromatic variables of colour, the hue is one of the most significant and intuitive. Although the CIE Uniform Colour Spaces (CIELUV, CIELAB) are frequently applied, dominant wavelength (λ_d), defined by the CIE 1931 (x, y) colorimetric system, remains as a useful representative parameter for hue when the colour in wines or any other foodstuff is defined. Colour stimuli of constant λ_d perceived under similar conditions would be said to have the same hue (Wyszecki & Stiles, 1982).

A general graphical procedure to calculate λ_d, valid in the Spanish Regulations (Presidencia del Gobierno, 1981), is usually applied. An interpolation method, which makes use of tables from Judd (1933), is utilized also. However, both methods lack accuracy or were tedious. Therefore, it would be useful to find an equation that gives λ_d values with an error, if possible, lower than the value generally accepted, *c.* 1 nm.

Piracci & Spera (1986) have proposed a five-grade polynomic equation with the distance, d, between the P_o point (λ_d = 700–770 nm) and the L point (which corresponds to the λ_d value for the P sample point) on the spectrum locus (Fig. 1) as independent variable. In the present paper, some equations for the estimation of λ_d are obtained, applying a nonlinear regression method. The purpose is to find an adequate computational expression as an alternative to the graphical procedure.

MATERIALS AND METHODS

Materials

Samples

Spanish red and rosé wines (109 samples), made in diverse Spanish regions, selected at random among the whole wine production, have been considered. There are wines from Origin Appellations, certified and experimental wines, young and aged wines. All the wines were produced from 1978 to 1988 vintages. Sample selection has been as diverse as possible to assure a sufficient representation of all the red grape varieties.

Referenced data for 66 samples of red and rosé wines have also been taken into account (Table 1).

Apparatus

Experimental absorbances were measured in a Bausch

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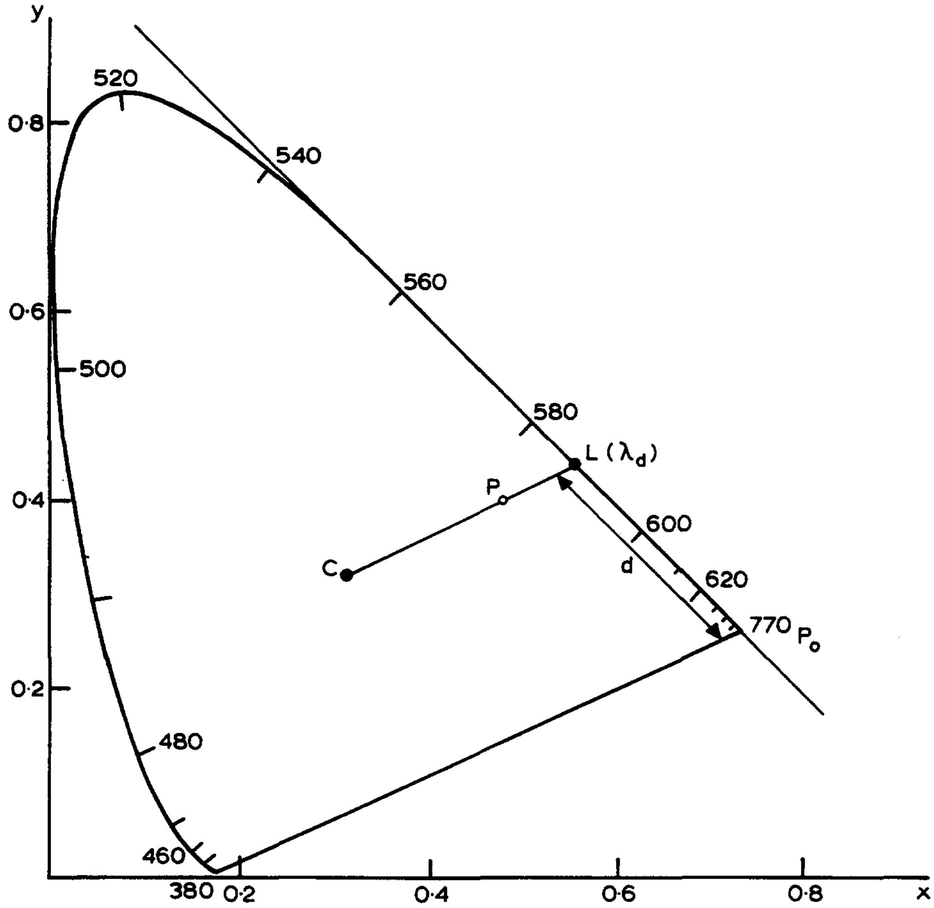

Fig. 1. CIE 1931 (x, y) chromatic diagram used to obtain λ_d.

& Lomb 'Spectronic 2000' spectrophotometer provided with a continuous X–Y recorder 333508. 'Hellma' precision glass cells with 1, 2, 5 or 10 mm pathlengths were used, according to the colour of sample. Because of the colloidal structure of wine, dilutions must be avoided. Data and statistical analyses were processed on a Digital VAX–11/785 computer.

METHODS

Absorbance measurements of the 109 Spanish wine samples were carried out within a time interval of 1 h after the bottles were opened; this action avoids the effect of colour instability with time elapsed (Heredia & Guzmán, 1988).

Table 1. Wine samples taken from the references

Number of samples	Code in the reference paper	Reference
4	A, B, A–B, A–B	Piracci & Spera (1986)
12	'Grenache' to 'Grignolino' 'Burger', California, in Table 1	Winkler & Amerine (1938)
2	9077, 9078	Ough *et al.* (1962)
16	34–36, 38–46, 48–51	Amerine *et* al. (1959)
8	All the wines in Table 2	Little (1977)
3	Wines 1 (pH 3·3), 2 (pH 3·3), 2 (pH 1·2), in Table 4	Little (1976)
21	All the wines in Table 2	Ough & Amerine (1967)

The Official Method for calculating chromaticity coordinates presents significant errors (Heredia & Guzmán, 1990). So the method used to compute chromatic parameters was the CIE 1931 (x, y) Colorimetric System (CIE, 1986).

Considering λ_d as a function of the slope of the straight line CL (Fig. 1) the derivative-free nonlinear regression method, DFNR (Ralston, 1981) has been applied. DFNR estimates, by means of an iterative algorithm, the characteristic coefficients of a specified nonlinear function for the maximum likelihood estimation. The residual sum of squares, between predicted and observed values, and the estimated square error, are reputable indices of the accuracy of the function.

RESULTS AND DISCUSSION

Piracci & Spere (1986) proposed the following five-grade polynomic equation:

$$\lambda_d = 656{\cdot}0675394 - 901{\cdot}2407644d + 6510{\cdot}818017d^2 - 27595{\cdot}00193d^3 + 59384{\cdot}29009d^4 - 51248{\cdot}46971d^5 \qquad (1)$$

where d had been defined above.

It is easy to understand that dominant wavelength could be expressed as a function of the chromaticity coordinates (x_L, y_L) or as a function of the slope (m) of the straight line CL (Fig. 1). After testing a great number of feasible exponential expressions, the following equation was chosen:

$$\lambda_d = 731{\cdot}3360e^{2{\cdot}0430{\cdot}x_L} - 4326{\cdot}7800x_L^{1{\cdot}6170} \qquad (2)$$

because it showed the least estimated mean square error for the tested exponential equations.

Residuals for 120 values of λ_d, obtained from 580 to 699 nm (the zone where all the red and rosé wines are included) were studied. It was inferred that several functions with the form of a polynomic quotient (Table 2) presented the minimum estimated mean square error and the highest correlation between predicted and observed values. The simplest among these equations was

$$\lambda_d = \frac{616{\cdot}5372 + 7193{\cdot}0947m + 18360{\cdot}3963m^2 - 396{\cdot}3129m^3}{1 + 11{\cdot}9328m + 31{\cdot}7620m^2} \qquad (3)$$

Table 2. Selected polynomic equations and their statistics

a	b	Degrees of freedom	Residual sum of squares	Estimated mean square error
2	2	115	60·3363	0·5247
3	2	114	42·5975	0·3737
3	3	113	42·3354	0·3747
4	2	113	42·3055	0·3744
4	3	112	42·2698	0·3774

a: degree of the numerator.
b: degree of the denominator.

Table 3. Statistics for eqns (1), (2) and (3) in the wines tested

Equation	n[a]	Residual sum of squares	Estimated mean square error
(1)	109[b]	145·8607	1·4161
(2)	109[b]	719·8905	6·8561
(3)	109[b]	2·3699	0·0230
(1)	66[c]	71·3879	1·0816
(3)	66[c]	1·3196	0·0200

[a] n = number of samples.
[b] Spanish wines.
[c] Wines from references.

The polynomic expression of the numerator must be at least of grade three for reaching an adequate precision.

Equations (1), (2) and (3) have been checked for two sample groups. One of them was formed by 109 Spanish red and rosé wines; the other group, 66 samples, was formed with the data previously referenced in the reference list. In Table 3, global statistics (residual sum of squares, mean square error) are summarized for each equation and each group of samples. In Figs 2 and 3,

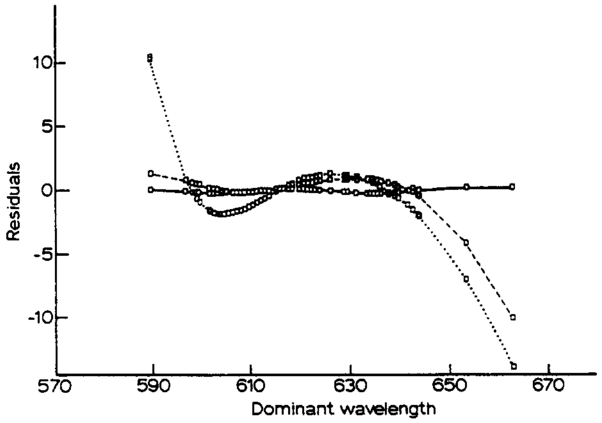

Fig. 2. Plot of residuals vs. reference λ_d for the tested equations (Spanish wines): ········, eqn (1); – – – –, eqn (2); ———, eqn (3).

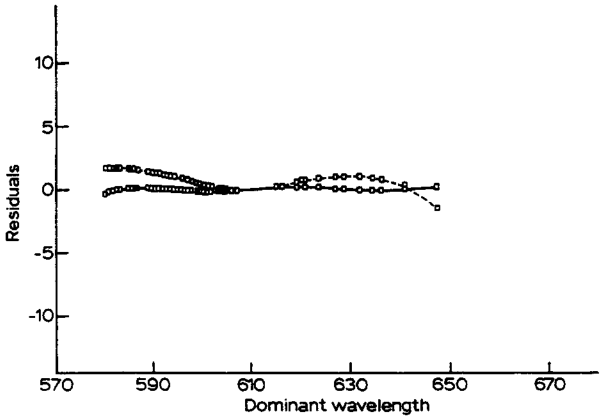

Fig. 3. Plot of residuals vs. reference λ_d for the tested equations (bibliographic data): – – – –, eqn (1); ———, eqn (3).

the variation of residual values, δ, with λ_d for eqns (1), (2) and (3), is shown.

It can be observed that, although eqn (1) shows an acceptable agreement in most samples (λ_d values for 'normal' red wines oscillate between 600 and 640 nm), for a few samples the λ_d differences become higher than 1 nm (e.g. for some young rosé wines, λ_d < 600 nm, made in Andalusia, $\delta \approx 4$ nm; and for some strongly coloured red wines or 'teinturiers' with λ_d > 660 nm, $\delta \approx 10$ nm). The exponential eq. (2), as the same authors noted (Piracci & Spera, 1986), does not seem suitable for the desired purpose, above all for the strongly coloured red wines. Equation (3) shows differences of less than 0·3 nm, so it is this equation that we propose for calculating the dominant wavelength of red and rosé wines. It is really a simple equation, where the independent variable (slope, *m*) can be directly calculated from the CIE 1931 (*x*, *y*) chromaticity coordinates of the colour point (sample point) and from those of the illuminant point (x_c, y_c) ($m = (y-y_c)/(x-x_c)$). So equation (3) is better than eqns (1) and (2) for wine or any foodstuff whose chromatic coordinates are studied within the section of the diagram bounded by the source and the range in the locus between 580 and 770 nm. For the wines with the shortest and largest λ_d (rosé and strongly coloured wines, respectively), the use of eqn (3) is clearly an improvement.

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