THE COLOR OF WINE: A HISTORICAL PERSPECTIVE. II. TRICHROMATIC METHODS

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ABSTRACT

The trichromatic theory was applied to wines at the end of the 1930s. Trichromatic co-ordinates, dominant wavelength, purity and luminance were determined. The Munsell system and the Lovibond method, which had industrial applicability, were compared with the simplified methods proposed by the L'office Internationale de la Vigne et du Vin (OIV). These methods are official in Spanish food regulations on wine analysis. The CIE recommendations, through the weighted ordinate method, set up the colorimetric parameters for wines, such as hue, lightness, purity or saturation, differences of color, perceptibility. Lately, attempts have been made to correlate the chromatic properties of wines with composition, origin, aging and sensory evaluation. Some authors have studied the reliability of the OIV methods versus the more rigid recent CIE methods. Improved formulae for the computation of dominant wavelength and outstanding correlations among sensorial scores, chromatic parameters and anthocyanins (polyphenols) content of wines have been established.

INTRODUCTION

As had been established in a campaign article (Heredia and Guzmán-Chozas 1993) chromatic methods based on direct spectral evaluations, in spite of being useful in the measurements of color variation in wine, show undoubted deficiencies with regard to the definition and characterization of color.

Adequate integration and visible absorption spectra have need of trichromatic methods, found in mechanisms of color vision by luminous stimuli. It is considered that any color may be matched by means of an appropriate mixture of three primary colored stimuli.

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The application of trichromatic theory to the color study of wines provides a number of possibilities in research of their optical properties and a more accurate chromatic characterization, through the several methodologies supported by organizations, such as the *Commission Internationale de l'Eclairage*, (CIE 1986).

TRICHROMATIC STIMULI

Winkler and Amerine (1938a,b) were the pioneers in the application of trichromatic theory to wine color. They considered the basic parameters: trichromatic coefficients (chromaticity coordinates), dominant wavelength (λ_d), purity and luminance. Likewise, they compared their results with the Wine-colorimeter of Salleron and they found:

(1) a lack of precision, overall in strongly colored wines, leading to errors of 10-25%
(2) a correct illumination seemed as not possible
(3) the colored specimens did not have an uniform intensity

Moreover, they studied the effect of diverse factors, as grape variety, the aging process, etc., and concepts as "brilliance" and "brightness" were differentiated. Afterwards, a number of authors made clear the importance of trichromatic systems for evaluating the color of wines (Little and MacKinney 1966; Joslyn and Little 1967; Francis 1969; Little and Liaw 1974; Kapustina *et al.* 1976; Roubert 1976; Timberlake 1981; Piracci 1984).

"Color in wines is composed of four basic colors: blue, green, yellow and red". This simple assertion from Villforth (1958) was the basis for his proposal of a color index for indicating the percentage (%) of light absorption at 538 nm, through 1 mm pathlength. The technique consists of measuring the transmittances with several filters:

(1) 420-490 nm, for blue
(2) 530-550 nm, for green
(3) 570-620 nm, for yellow
(4) 665-750 nm, for red

The Munsell system has been applied for chromatic evaluation of wines and other foods extensively (Jacobs 1938; Kramer and Twigg 1959; National Canners Association Research Laboratories 1968; Bardavio 1970; Little 1976). Amerine *et al.* (1959) have used the Munsell method to study the color of white and red wines to compare their results with those obtained through the use of different colorimeters.

Sambuc and Naudet (1965) emphasized the importance of color in foodstuffs, and they studied the use of the XYZ systems with illuminant C as a reference. These authors proposed replacing the CIE methods by simplified methods, based on the selection of the most representative wavelengths. Furthermore such methods would have an instrumental advantage, since only necessary would be a simple colorimeter equipped with four color filters. They applied the standard color scales frequently used, as the Gardner or FAC scales. Previously, they had determined the trichromatic characteristics of the standard filters by using the Lovibond method and by means based on transformation diagrams. But

(1) in most cases these methods have been established from a set of given filters without correcting for their probable inaccuracy

(2) trichromatic determinations were only useful to measure chromaticities through filter combinations, and moreover they did not offer lightness differences.

The Lovibond method, founded on the use of three sets of glass filters (red, blue and yellow) (Anonymous 1939), was devised at first for the controlling for beer color (Ingle 1962; Egan *et al.* 1981), and it has also been applied to fats and oils (Pomeranz and Meloan 1978). The method estimates lightness differences by using grey filters, but it presented some instrumental difficulties and disability to obtain the inverse transformation. Because of them, Sambuc and Naudet (1965) treated the calculation of trichromatic coordinates of filters and their combinations.

The international methods for wine color analyses, proposed by the "L'Office Internationale de la Vigne et du Vin", OIV, are based on studies of the color of edible oils (Presnell 1949; Sambuc and Naudet 1956, 1965; Bigoni 1963; Stella 1966). These authors proposed diverse expressions (Table 1) to obtain tristimuli values (X,Y,Z), which are valid in the predominant color region, from the simplified Selected Ordinate Method of Hardy (1936).

These formulae have been included in national and international regulations on analysis of wines (Presidencia del Gobierno 1977; 1981; CEE 1990).

Some errors found in the earlier equations (Table 1) to calculate tristimuli values have been demonstrated recently by Heredia and Guzmán (1991). Negueruela and Echávarri (1988; 1989) and Negueruela *et al.* (1988; 1990) have proposed a modification of the OIV method for red wines and their mixtures, by using the Standard Illuminant D_{65} and the CIE Standard Observer 1964 (x_{10}, y_{10}), defined for vision angles greater than 4°. They have obtained equations dependent on absorbances at 420, 520 and 620 nm, considered by Glories (1984) as the most significant in wines.

TABLE 1.
EQUATIONS TO OBTAIN TRISTIMULI VALUES (X, Y, Z)

(1) *Presnell (1949):*

$$X = 0.20\ T_{445} + 0.15\ T_{555} + 0.65\ T_{600}$$

$$Y = 0.10\ T_{445} + 0.70\ T_{555} + 0.20\ T_{600}$$

$$Z = 1.20\ T_{445} + 0.06\ T_{555}$$

(2) *Sambuc and Naudet (1956)*, for the illuminant A:

$$X = 0.46\ T_{624.2} + 0.33\ T_{551.8} + 0.19\ T_{444.4}$$

$$Y = 0.20\ T_{624.2} + 0.63\ T_{551.8} + 0.17\ T_{495.2}$$

$$Z = 0.24\ T_{495.2} + 0.94\ T_{444.4}$$

(3) *Bigoni (1963)*, for the illuminant A:

$$X = 0.04\ T_{660} + 0.40\ T_{625} + 0.37\ T_{550} + 0.19\ T_{445}$$

$$Y = 0.19\ T_{625} + 0.64\ T_{550} + 0.17\ T_{495}$$

$$Z = 0.18\ T_{495} + 0.82\ T_{445}$$

(4) *Stella (1966)*, for the illuminant C:

$$X = 0.04\ T_{660} + 0.39\ T_{625} + 0.36\ T_{550} + 0.18\ T_{445}$$

$$Y = 0.19\ T_{625} + 0.64\ T_{550} + 0.17\ T_{495}$$

$$Z = 0.21\ T_{495} + 0.97\ T_{445}$$

(5) *OIV (1969)* equations:

$$X = 0.42\ T_{625} + 0.35\ T_{550} + 0.21\ T_{445}$$

$$Y = 0.20\ T_{625} + 0.63\ T_{550} + 0.17\ T_{495}$$

$$Z = 0.24\ T_{495} + 0.94\ T_{445}$$

HUE

Little (1976) defined hue as the attribute by which a color is identified as *red, yellow, green*, etc., so it is closely related with dominant wavelength (λ_d).

Dominant wavelength (λ_d), as a representative parameter of the hue or tint of color, is very important in the chromatic study of red wines. Several authors (Winkler and Amerine 1938a; Ough *et al.* 1962) have demonstrated the interest of λ_d for the color characterization. For rose wines, dominant wavelength takes values lower than for red wines (up to 40 nm of difference); so, we can think this could be a useful discriminant parameter (Amerine and Winkler 1941). Amerine *et al.* (1959) studied dominant wavelengths in white and rose wines from California. Sudraud (1958) pointed out that the ratio A_{420}/A_{520} could be used as a measure of hue changes related to dominant wavelength. Ough *et al.* (1962), by using a simplified method, found a linear relation between log 1/%X, log 1/%Y, log 1/%Z and color intensity. Beginning from three samples (purple, λ_d = 505 nm; orange, λ_d = 592 nm; red, λ_d = 611.2 nm) the authors prepared different mixtures.

Beginning from three standard wines (Cabernet, dark purple-red; Burgundy, dark red; and rose, light orange-red) and their blends, Berg *et al.* (1964) found an agreement between λ_d values and the response to hue of the panelists, that was directly related with the square root of the increase of dominant wavelength ($\Delta\lambda_d$).

By means of a graphic procedure, the distance between P_0 (λ_d: 700-770 nm) and P (λ_d of the sample) was measured by Piracci and Spera (1986). From this distance they proposed to apply a five-grade polynomic equation to calculate the dominant wavelength (λ_d) of a red wine. A novel polynomic quotient formula to calculate dominant wavelength for color of red wines has been recently proposed (Heredia and Guzmán, 1992).

LIGHTNESS

According to Little (1976) the lightness could be considered as the apparent proportion of incident light reflected or transmitted by the object on a scale that goes from the white or colorless to black. Lightness data for 33 rather different white wines and 18 red wines have been offered (Amerine *et al.* 1959). It was proved that rose wines had greater lightness values than red wines (Amerine and Winkler 1941). Approximations of percent brightness and dominant wavelength and some blending applications with red wines have been carried out (Ough *et al.* 1962).

When the color points reach values which correspond to luminosity (Y) values of $Y \simeq 2$, the trends of the color points to move in parallel with the spectrum locus, as well as the hue to shift from purple towards orange-red stopped (Kampis and Asvany 1985); that is, the spectral colors of the monomer and polymer pigments of red wines whose luminosity (Y) surpass the value Y = 2 may not differ significantly. But in dark red wines, whose luminosity (Y) was below 2, the trend of the shift of color points during storage would result in an alignment of these points away from the achromatic point. As a consequence of this behavior, the color points move to higher dominant wavelength (λd), and they were placed in the corner of the "color triangle". This event is owing to the polymerization of pigments during the storage period.

PURITY

Little (1976) defines purity or saturation as the proportion of chromatic content in the total perception; it is also the level of difference from the neutral or grey point of the same lightness value. The Munsell chroma scale is founded on the second definition. In the paper published by Amerine *et al.* (1959), data of percentage of purity for diverse red and white wines (Sauterne, Muscatel, Sherry, Burgundy) are given. Rose wines have purity values lower than red wines (Amerine and Winkler 1941).

COLOR DIFFERENCES

Berg *et al.* (1964) proposed a spectrophotometrical method based on visual comparisons of artificial blends to predict perceptibility of the difference between transmittance and dominant wavelength among red wines. In the CIELAB color space, the distance between two distinguishable stimuli by a well trained eye is 0.1 units of difference of color (ΔE) (when optimal conditions are applied). But for the human eye in ordinary circumstances, a distance of 1 between the stimuli to be distinguishable is more appropriate. Negueruela and Echávarri (1983) have calculated in Rioja wines ΔE to check the reliability of the simplified methods proposed by OIV (1969). They observed high values for ΔE, between 7 and 15 units, when young red wines were tested. In wines aged more than two years, the color differences (ΔE) oscillated around 1-2 units, very near the perceptibility limit.

SENSORY EVALUATION

The human eye is extraordinarily sensitive to small differences in colors, and the development of a rational color nomenclature would be desirable (Amerine and Roessler 1983). Otherwise, terms such as *scarlet, brilliant scarlet, flashing scarlet, bright ruby scarlet, limpid scarlet, ruby scarlet* and *scarlet-toned* seem impossible to be distinguishable (Peynaud 1984).

Until now, not many studies about sensory evaluation of wines and its relation with the chromatic parameters have been carried out (Crawford *et al.* 1958; Singleton and Ough 1962; Pangborn *et al.* 1963; Little 1973; Amerine and Roessler 1983; De Rosa 1985; Castino *et al.* 1990). Ough and Berg (1959) published a pioneer study on wines regarding the possibility of a correlation between chromaticity qualities and the scores given by experienced panelists under various light sources. Studies involving rose wine color preferences, by comparing the scores given by experienced and inexperienced panels (consumers panel), have been carried out too (Ough and Amerine 1967). Both groups showed similar patterns, but there was significantly more consistent preferences with the experienced panel.

Correlations between the characteristics of the objective (instrumental) measurements and visual sensation have been established. By means of triangular and ranking tests the agreement between the human eye and instrumental sensitivities have been studied. Scores from 0 to 30 were then compared with anthocyanin content, color intensity, hue and tristimuli values (Kerenyi and Kampis 1984). Casp and Bernabéu (1987a,b) develop sensory characterization attempts using rose, white and red wines; but they did not correlate sensory scores with objective (instrumental) methods.

There are a number of general studies about visual perception that must be considered when a program on sensory evaluation of color is developed. Studies on visual efficiency (MacAdam 1935a,b) and subjective ability for color matching (Newhall *et al.* 1957); the influence of the metamerism and fusion of primaries on color differential threshold (Hita *et al.* 1976; Lozano 1979) have been made. Even considerations about the influence of the time interval between stimuli perception discrimination experiments, have been taken into account (Romero *et al.* 1986)

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