Measurement of Wine Vinegars' Color: Application of the Characteristic Vector Method

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As there is no official method to measure the color of wine vinegar, the aim of this work is to propose a quick and simple method to do so with minimum error. Vector analysis was tested and proved to be applicable to the reconstitution of vinegar transmittance spectra. When spectrophotometric measurements are made with 0.2 cm path length cells, the use of three characteristic vectors is sufficient for a close approximation. Determination of transmittance at only three wavelengths, 440, 530, and 590 nm, is necessary to obtain the three coefficients necessary to reconstitute a vinegar's spectrum and to obtain the tristimulus chromatic characteristics. The color coordinates of each vinegar have been calculated on the basis of these results.

Keywords: *Wine vinegar; color; characteristic vector analysis; tristimulus colorimetry*

INTRODUCTION

Color is an important aspect of vinegar quality because of its relevance in sensory analysis and as indicator of processes, such as oxidation and aging.

Each winery producing high-quality traditional vinegar wants to have its own standardized color that may serve to identify the brand. As a final step in the production of sherry wine vinegars, color is adjusted before bottling. The adjustment is carried out by the addition of a small quantity of must caramel, which, if it is added in excess, would give the product a bitter taste.

In the industry producing vinegars by quick methods using Fring's acetator, the study of color has an additional interest, as color is not stable in the final product once the bottle has been opened. In fact, the contact with oxygen produces an undesirable brown color, which is detrimental to quality, so the industry is making an effort to study the color of vinegars and to find possible solutions to this problem.

When assessing the sensory profile of vinegars, some authors use four descriptors concerned with color, color intensity and yellow, gold, and amber components (Gerbi et al., 1997), whereas they use only three to describe taste, indicating the relative importance that color has in the total appreciation of the product. However, in place of such subjective methods, it is desirable and of major interest to have an objective, simple, and quick method for measuring the color of vinegars.

Methods for analyzing chemical or physical parameters of vinegars have been traditionally adapted from those for wines as there are many similarities. At this time, there is no official method for measuring the color of vinegars and usually the official method for wines is accepted. However, its validity even in wines has been discussed (Barros and Ribeiro, 1993; Heredia Mira and Guzmán Chozas, 1986; Negueruela and Echávarri, 1983), and it does not seem adequate for application to vinegars in its original form.

The present work has the aim of setting up a method to measure the color of vinegars with greater precision and simplicity than the official method for wines.

MATERIALS AND METHODS

Samples. Ninety-nine samples of vinegar from almost every winery producing wine vinegar in the south of Spain were subjected to study. The group of samples includes vinegars made both by traditional slow methods and by quick methods.

Apparatus. An HP8452A UV diode array spectrophotometer was used to scan the spectra of the samples over the range 380−770 nm employing 0.2 cm path length cells.

Procedure. The proposed method is based on the weighted ordinate method recommended by the Commission Internationale de l'Éclairage (Verger-Schunn, 1994). This method is applied over the whole visible spectrum, 380−770 nm, at 1, 5, or 10 nm intervals, using the following equations to calculate the tristimulus values:

$$X = k\sum_{\lambda=I\lambda\eta}^{\Lambda\Lambda\eta}\tau_\lambda L_\lambda \bar{x}_\lambda \Delta\lambda$$

$$Y = k\sum_{\lambda=I\lambda\eta}^{\Lambda\Lambda\eta}\tau_\lambda L_\lambda \bar{y}_\lambda \Delta\lambda \qquad (1)$$

$$Z = k\sum_{\lambda=I\lambda\eta}^{\Lambda\Lambda\eta}\tau_\lambda L_\lambda \bar{z}_\lambda \Delta\lambda$$

k is a normalizing factor, τ_λ is the spectral transmittance of the sample, L_λ is the spectral emission of the illuminant

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chosen, $\bar{x}_\lambda$, $\bar{y}_\lambda$, and $\bar{z}_\lambda$ are the color-matching functions of the standard observer selected, and $\Delta\lambda$ is the measurement interval, which can be 10 nm for wines, as we have checked.

From these expressions, and for one measured transmittance spectrum, we can obtain the different tristimulus values corresponding to each illuminant and each standard observer.

The CIELAB formula for color specification is used in this work (CIE, 1986). Its coordinates as functions of the CIE tristimulus values are

$$L^* = 116[F(2) - 0.1379]$$

$$a^* = 500[F(1) - F(2)]$$

$$b^* = 200[F(2) - F(3)]$$

in which

$$F(i) = G(i)^{1/3} \qquad \text{if } G(i) > 0.008856$$

or

$$F(i) = 7.787G(i) + 0.1379 \qquad \text{if } G(i)^2 \le 0.008856$$

In $F(i)$

$$G(i) = T(i)_e/T(i)_n \qquad \text{for } i = 1, 2, 3$$

where

$$T(1) = X,\ T(2) = Y, \text{ and } T(3) = Z$$

The subscripts e and n refer to the sample and to the specified reference white, respectively.

Coordinate a^* is related to red color if $a^* > 0$ and to green color if $a^* < 0$. Analogously, coordinate b^* is related to yellow color if $b^* > 0$ and to blue color if $b^* < 0$.

The cylindrical coordinates L^*, C^*, and h^*, where

$$C^* = (a^{*2} + b^{*2})^{1/2}$$

$$H^* = \text{arc tg } (b^*/a^*)$$

are qualitatively related to the psychological attributes of color: the color difference between two different colors is

$$\Delta E^*_{a,b} = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \text{ in CIELAB units}$$

L^* (lightness) is the lightness of a colored object judged relative to the lightness that appears as white. C^* (chroma) is the chromaticity of a colored object judged relative to white. h^* (hue) is the attribute of appearance by which a color is identified according to its resemblance to red, yellow, green, blue, or a combination of two of those in sequence.

A mathematical statement of the characteristic vector analysis (Lebart et al., 1985) might be given as follows. Response data τ_λ (transmittance spectrum) are available for r (40) levels of the variable λ (wavelength) and can be plotted as a response curve. For each sample, then, the r values of τ_λ constitute a one-row r-column vector of response data. For n sample sets of data, the response vectors can be arrayed to form a data matrix of n rows and r columns.

It is possible to find a set of p characteristic vectors ($p < r$), which, when added in the proper amounts to the mean response vector, will adequately approximate any of the original family of response vectors. The result is that the components of the generic vectors (i.e., the transmittance spectra) can be expressed as

$$\bar{\tau}_\lambda = M_1V_{1,\lambda} + M_2V_{2,\lambda} + \ldots + M_pV_{p,\lambda} \qquad (2)$$

where $\bar{\tau}_\lambda$ represents the components of the mean vector, $V_{i,\lambda}$ the components of the characteristic ith vector, and M_i the specific coefficients, called scalar multiples, of each reconstituted vector.

This analysis must be applied to a large number, n, of experimental curves. The mathematical procedure calculates the M_i coefficients to reconstitute each of these curves and the percentage of the variability among the family of homologous response curves explained for each characteristic vector.

$$X = k\sum_{\lambda=I\lambda\eta}^{\Lambda\Lambda\eta}(\bar{\tau}_\lambda + M_\Theta V_{\Theta\epsilon\lambda} + M_\theta V_{\theta\epsilon\lambda} + \ldots + M_{\alpha;\epsilon\lambda})\bar{L}_\lambda\bar{x}_\lambda\Delta_\lambda$$

If these expressions for τ_λ are substituted into eq 1 for the tristimulus values, any of them, for example, X, has the expression that we can write as

$$X = k\sum_{\lambda=I\lambda\eta}^{\Lambda\Lambda\eta}\bar{\tau}_\lambda\bar{L}_\lambda\bar{x}_\lambda\Delta_\lambda + M_\Theta k\sum_{\lambda=I\lambda\eta}^{\Lambda\Lambda\eta}V_{\Theta\epsilon\lambda}\bar{L}_\lambda\bar{x}_\lambda\Delta\lambda + \ldots + M_{,}k\sum_{\lambda=I\lambda\eta}^{\Lambda\Lambda\eta}V_{;\epsilon\lambda}\bar{L}_\lambda\bar{x}_\lambda\Delta\lambda \qquad (3)$$

because the M_i coefficients are independent of the wavelength for any single reconstituted curve.

Calling

$$X_\chi = k\sum_{\lambda=I\lambda\eta}^{\Lambda\Lambda\eta}V_{\chi\epsilon\lambda}\bar{L}_\lambda\bar{x}_\lambda\Delta\lambda$$

we can write eq 3 as

$$X = X_0 + M_1X_1 + M_2X_2 + \ldots + M_pX_p \qquad (4)$$

where X_0 is the tristimulus value corresponding to the mean transmittance spectrum and X_i could be considered the theoretical tristimulus values of each characteristic vector. Analogous expressions are obtained for the Y and Z tristimulus values.

If the results are to be applied to spectra from other samples, different from the previous ones, it is necessary to calculate the corresponding M_i coefficients. To do this the $\tau_{\lambda i}$ transmittances at as many wavelengths as characteristic vectors appear in eq 2 must be measured, and the following system of equations must be solved:

$$\tau_{\lambda 1} = M_1V_{1,\lambda 1} + M_2V_{2,\lambda 1} + \ldots + M_pV_{p,\lambda 1}$$

$$\tau_{\lambda 2} = M_1V_{1,\lambda 2} + M_2V_{2,\lambda 2} + \ldots + M_pV_{p,\lambda 2} \qquad (5)$$

$$\tau_{\lambda p} = M_1V_{1,\lambda p} + M_2V_{2,\lambda p} + \ldots + M_pV_{p,\lambda p}$$

where the values of $V_{j,\lambda i}$ are the results of previous statistical study.

Because the M_i coefficients calculated from eq 5 are functions of the measured transmittances, $\tau_{\lambda i}$, they can be substituted into eq 4, giving this final result:

$$X = C_{0x} + C_{1x}\tau_{\lambda 1} + C_{2x}\tau_{\lambda 2} + \ldots + C_{px}\tau_{\lambda p} \qquad (6)$$

By analogous argument for Y and Z, we may write

$$Y = C_{0y} + C_{1y}\tau_{\lambda 1} + C_{2y}\tau_{\lambda 2} + \ldots + C_{py}\tau_{\lambda p}$$

$$Z = C_{0z} + C_{1z}\tau_{\lambda 1} + C_{2z}\tau_{\lambda 2} + \ldots + C_{pz}\tau_{\lambda p}$$

that express the tristimulus values directly as a function of the measured transmittances. The color coordinates, in any CIE system, can be obtained from these tristimulus values.

The analysis of the characteristic vectors has been carried out following the adaptation of the method made by Simonds (1963), using our own software.

After calculating the first four characteristic vectors, and, in view of the high percentage of the variability of data

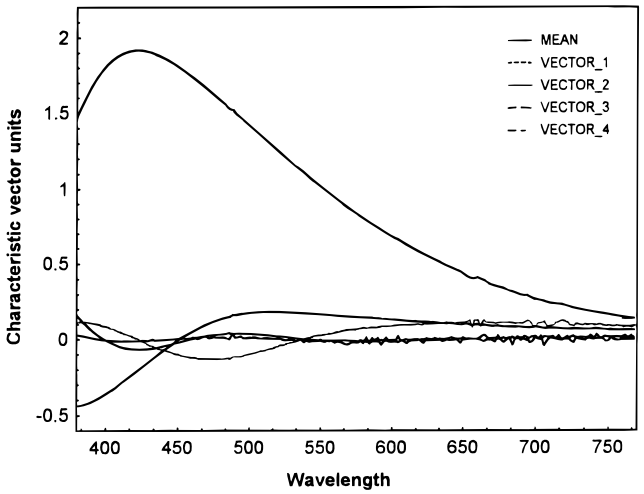

Figure 1. Mean vector and four characteristic vectors obtained.

explained by them, we carried out four reconstitutions of each spectrum, starting with the mean vector and the first characteristic vector and adding the corresponding next characteristic vector to each following reconstitution and multiplying each vector i by its M_i coefficient provided by the mathematical method used.

On the basis of the experimental and reconstituted spectra, the color coordinates have been calculated using the CIE 1964 standard observer and the illuminant D65, following the CIE recommendations (CIE, 1986).

Theoretically, any set of p wavelengths could be used to obtain the transmittances $\tau_{\lambda i}$ in eq 6, but we have found that this is not so and that it is necessary to select, using a computer scanning process, those which give the best results for calculating the tristimulus values (Ayala, 1993).

Using the coordinates obtained on application of the CIE method to the experimental spectra as reference coordinates, color differences have been calculated, in CIELAB units, between these coordinates and both those obtained from the reconstituted spectra and those calculated from tristimulus values obtained using eq 5.

RESULTS AND DISCUSSION

Figure 1 shows the mean vector and the four characteristic vectors obtained in the process. The spectra of two vinegars, experimentally measured and reconstituted with three characteristic vectors, respectively, are displayed in Figure 2 as examples.

After analyzing these results, we concluded that the reconstitution of spectra obtained from three characteristic vectors was sufficient for our project, because the color differences were lower than 1 CIELAB unit for each of the 99 vinegars.

After calculating the tristimulus values corresponding to the mean vector and the first three characteristic vectors and substituting them into eq 4, we obtained the following expressions for the tristimulus values of any vinegar:

$$X = 75.810 + 90.541M_1 + 9.847M_2 + 4.320M_3$$

$$Y = 79.413 + 103.216M_1 + 14.886M_2 + 1.552M_3 \quad (7)$$

$$Z = 59.619 + 189.378M_1 - 1.251M_2 - 8.843M_3$$

To obtain the best results using eq 6, we searched for wavelength triads using scans around 450, 550, and 600 nm, because the best results had been obtained in these

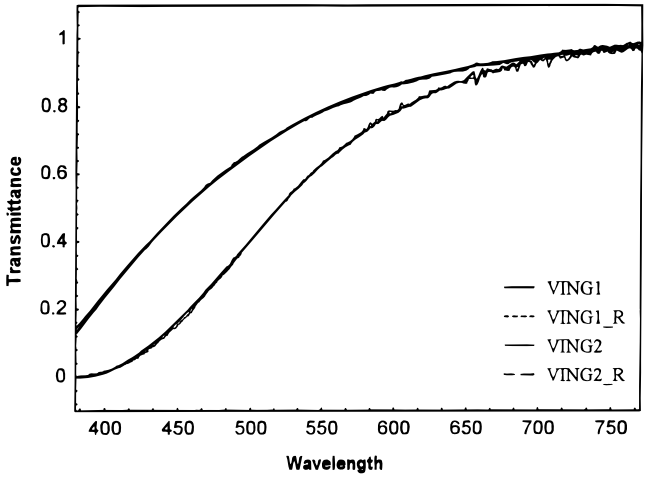

Figure 2. Experimentally measured and reconstitued spectra of two vinegars.

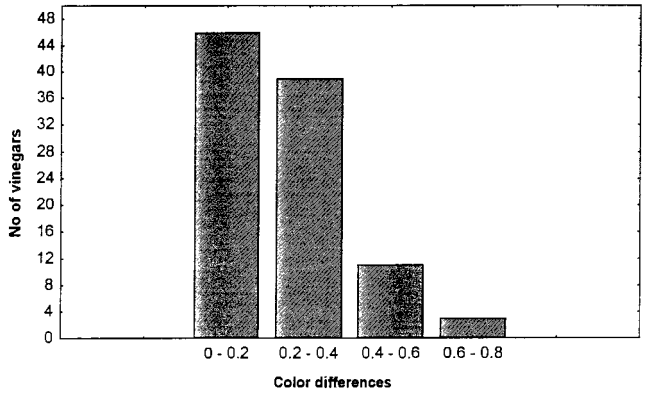

Figure 3. Frequency histogram of color differences with respect to the reference color coordinates.

areas of the spectrum in previous papers (Ayala et al., 1993; Juarez, 1991; Juarez et al., 1990). The wavelengths selected were 440, 530, and 590 nm and eq 5 becomes

$$\tau_{440} = 0.519 + 1.867M_1 - 0.073M_2 - 0.068M_3$$

$$\tau_{530} = 0.770 + 1.173M_1 + 0.180M_2 - 0.018M_3 \quad (8)$$

$$\tau_{590} = 0.870 + 0.740M_1 + 0.142M_2 + 0.085M_3$$

where τ_{440}, τ_{530}, and τ_{590} are the transmittances measured at these wavelengths.

Solving for M_1, M_2, and M_3 in eq 8 and substituting into eq 7, we find the following expressions for tristimulus values:

$$X = 16.432\tau_{440} + 9.237\tau_{530} + 66.270\tau_{590} + 2.511$$

$$Y = 5.333\tau_{440} + 57.668\tau_{530} + 34.652\tau_{590} + 2.084 \quad (9)$$

$$Z = 82.118\tau_{440} + 48.436\tau_{530} - 28.058\tau_{590} + 4.061$$

After the tristimulus values of the 99 vinegars were calculated from eq 9, their CIELAB color coordinates and the corresponding color differences with respect to the reference color coordinates were obtained. Figure 3 shows the frequency histogram of these color differ-

ences, being lower than 1 CIELAB unit for 100% of the vinegars, which improves on the previous result.

CONCLUSIONS

The characteristic vector analysis is applicable to the reconstitution of vinegar transmittance spectra, and the use of three of them is sufficient for close approximation when the spectrophotometric measurements are made with 0.2 cm path length cells.

To obtain the three coefficients necessary to reconstitute a vinegar spectrum, it is sufficient to measure the transmittance at three wavelengths: 440, 530, and 590 nm.

The tristimulus values of these vinegars, calculated for the illuminant D65 and the CIE 1964 standard observer, can be obtained by applying eq 9 directly to the values for the three mentioned transmittances.

The color differences between the coordinates thus obtained and those calculated by applying the CIE method to the experimental spectra are <1 CIELAB unit in 100% of the 99 vinegars used in this work. These color differences are small enough not to be noticed by eye when two samples in a glass cup are compared.

We suggest the use of 0.2 cm path length cells, in spectrophotometric measurements, eq 9 for the measurement of vinegar color, and comparison of these results with those obtained with the CIE 40 spectral measurements method whenever possible to test the accuracy of the method.

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