

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231556168>

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

ARTICLE in JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY · SEPTEMBER 1998

Impact Factor: 2.91 · DOI: 10.1021/jf980291j

CITATIONS

6

READS

29

6 AUTHORS, INCLUDING:



**María Carmen Garcia-Parrilla**

Universidad de Sevilla

78 PUBLICATIONS 2,136 CITATIONS

SEE PROFILE



**Ana M Troncoso**

Universidad de Sevilla

106 PUBLICATIONS 2,801 CITATIONS

SEE PROFILE



**Angel Ignacio Negueruela**

University of Zaragoza

34 PUBLICATIONS 514 CITATIONS

SEE PROFILE



**Francisco J. Heredia**

Universidad de Sevilla

190 PUBLICATIONS 3,303 CITATIONS

SEE PROFILE

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

M. Carmen García-Parrilla,<sup>†</sup> Fernando Ayala,<sup>‡</sup> J. Federico Echávarri,<sup>‡</sup> Ana M. Troncoso,<sup>†</sup>  
A. Ignacio Negueruela,<sup>§</sup> and Francisco J. Heredia<sup>\*,†</sup>

Área de Nutrición y Bromatología, Facultad de Farmacia, Universidad de Sevilla, c/ P. García González s/n, 41012 Sevilla, Spain, Laboratorio de Color de La Rioja, Universidad de La Rioja, Luis de Ulloa 20, 26004 Logroño, Spain, and Departamento de Física Aplicada, Facultad de Veterinaria, Universidad de Zaragoza, Miguel Servet 177, 50013 Zaragoza, Spain

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:

$$\begin{aligned} X &= k \sum_{\lambda=380}^{770} \tau_{\lambda} L_{\lambda} x_{\lambda} \Delta\lambda \\ Y &= k \sum_{\lambda=380}^{770} \tau_{\lambda} L_{\lambda} y_{\lambda} \Delta\lambda \\ Z &= k \sum_{\lambda=380}^{770} \tau_{\lambda} L_{\lambda} z_{\lambda} \Delta\lambda \end{aligned} \quad (1)$$

$k$  is a normalizing factor,  $\tau_{\lambda}$  is the spectral transmittance of the sample,  $L_{\lambda}$  is the spectral emission of the illuminant

\* Author to whom correspondence should be addressed (telephone 3454556761; e-mail heredia@fafar.us.es).

<sup>†</sup> Universidad de Sevilla.

<sup>‡</sup> Universidad de La Rioja.

<sup>§</sup> Universidad de Zaragoza.

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

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

or

$$F(t) = 7.787G(t) + 0.1379 \quad \text{if } G(t) \leq 0.008856$$

In  $F(t)$

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

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

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

$$h^* = \arctan(b^*/a^*)$$

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  $\tau_\lambda$  (transmittance spectrum) are available for  $r$  (40) levels of the variable  $\lambda$  (wavelength) and can be plotted as a response curve. For each sample, then, the  $r$  values of  $\tau_\lambda$  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

$$\bar{\tau}_\lambda = M_1 V_{1,\lambda} + M_2 V_{2,\lambda} + \dots + M_p V_{p,\lambda} \quad (2)$$

where  $\bar{\tau}_\lambda$  represents the components of the mean vector,  $V_{i,\lambda}$  the components of the characteristic  $i$ th 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.

$$X = k \sum_{\lambda=L\lambda\eta}^{\Lambda\Lambda\eta} (\tau_\lambda + M_\Theta V_{\Theta\epsilon\lambda} + M_\theta V_{\theta\epsilon\lambda} + \dots + M_{\alpha;\epsilon\lambda}) \bar{L}_\lambda \bar{x}_\lambda \Delta\lambda$$

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

$$X = k \sum_{\lambda=L\lambda\eta}^{\Lambda\Lambda\eta} \tau_\lambda \bar{L}_\lambda \bar{x}_\lambda \Delta\lambda + M_\Theta k \sum_{\lambda=L\lambda\eta}^{\Lambda\Lambda\eta} V_{\Theta\epsilon\lambda} \bar{L}_\lambda \bar{x}_\lambda \Delta\lambda + \dots + M_i k \sum_{\lambda=L\lambda\eta}^{\Lambda\Lambda\eta} V_{i;\epsilon\lambda} \bar{L}_\lambda \bar{x}_\lambda \Delta\lambda \quad (3)$$

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

Calling

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

we can write eq 3 as

$$X = X_0 + M_1 X_1 + M_2 X_2 + \dots + M_p X_p \quad (4)$$

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:

$$\begin{aligned} \tau_{\lambda 1} &= M_1 V_{1,\lambda 1} + M_2 V_{2,\lambda 1} + \dots + M_p V_{p,\lambda 1} \\ \tau_{\lambda 2} &= M_1 V_{1,\lambda 2} + M_2 V_{2,\lambda 2} + \dots + M_p V_{p,\lambda 2} \\ \tau_{\lambda p} &= M_1 V_{1,\lambda p} + M_2 V_{2,\lambda p} + \dots + M_p V_{p,\lambda p} \end{aligned} \quad (5)$$

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:

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

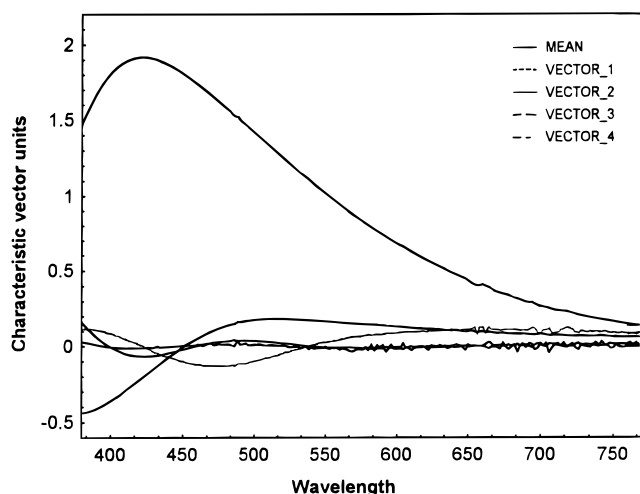
By analogous argument for  $Y$  and  $Z$ , we may write

$$\begin{aligned} Y &= C_{0y} + C_{1y} \tau_{\lambda 1} + C_{2y} \tau_{\lambda 2} + \dots + C_{py} \tau_{\lambda p} \\ Z &= C_{0z} + C_{1z} \tau_{\lambda 1} + C_{2z} \tau_{\lambda 2} + \dots + C_{pz} \tau_{\lambda p} \end{aligned}$$

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.

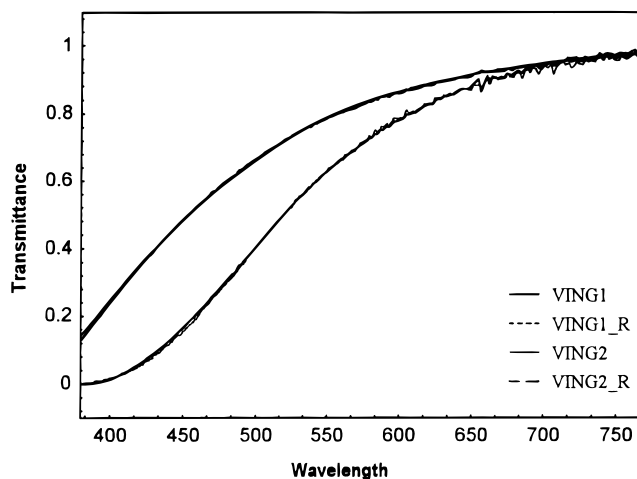
After calculating the tristimulus values corresponding to the mean vector and the first three characteristic vectors and substituting them into eq 4, we obtained the following expressions for the tristimulus values of any vinegar:

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

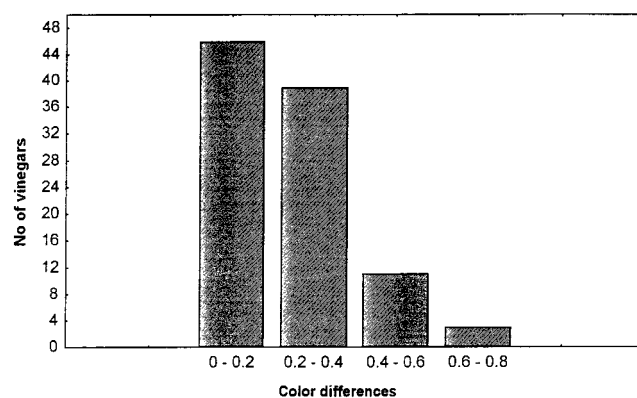
$$Y = 79.413 + 103.216M_1 + 14.886M_2 + 1.552M_3 \quad (7)$$

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

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 reconstituted 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; Juárez, 1991; Juárez 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  $\tau_{440}$ ,  $\tau_{530}$ , and  $\tau_{590}$  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.

## LITERATURE CITED

- Ayala, F.; Echávarri, F. J.; Juárez, M. C.; Negueruela, A. I. A Suggested New Colour of Red Wines Measuring Method. *Opt. Pura Apl.* **1993**, *26*, 533–541.
- Barros, P.; Ribeiro, M. Colorimetria no Vinho do Porto. Presented at the Seminario de Colorimetria Aplicada e Industrial, Exponor Porto, March 18–21, 1993.
- CIE. *Colorimetry*, 2nd ed.; CIE Publication 15.2; Vienna, 1986.
- Gerbi, V.; Zeppa, G.; Antonelli, A.; Carnacini, A. Sensory characterisation of wine vinegars. *Food Qual. Pref.* **1997**, *1*, 27–34.
- Heredia Mira, F. J.; Guzmán-Chozas, M. Evolución del análisis cromático en vinos. *Sem. Vitivinic.* **1986**, 2104–2105, 4959–4963.
- Juarez, M. C. Obtención de los espectros de absorbancias y transmitancias de vinos de Rioja utilizando un método de vectores característicos y su aplicación a la determinación del color de los mismos. Tesis Doctoral, Universidad de Zaragoza, 1991.
- Juarez, M. C.; Echavarri, J. F.; Negueruela, A. I. Reconstrucción del Espectro de Transmitancias de Vinos Rosados Mediante Vectores Propios y Aplicaciones Colorimétricas. Presented at the II Reunión Nacional de Optica. Santiago de Compostela, 1990.
- Lebart, L.; Morineau, A.; Fenelon, J. P. *Tratamiento Estadístico*; Marcombo: Barcelona, 1985.
- Negueruela, A. I.; Echavarri, J. F. Colorimetria en Vinos de Rioja. *Opt. Pura Apl.* **1983**, *16*, 97–106.
- Simonds, J. L. Application of Characteristic Vector Analysis to Photographic and Optical Response Data. *J. Opt. Soc. Am.* **1963**, *53*, 968.
- Verger-Schuun, A. *Practical Color Measurement*; Wiley: New York, 1994.

Received for review March 20, 1998. Revised manuscript received June 29, 1998. Accepted July 1, 1998.

JF980291J