Simplified Measurement of Virgin Olive Oil Color by Application of the Characteristic Vector Method

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ABSTRACT: There are several simplified methods to measure the color of virgin olive oils. However, their reliability is questionable, as they provide errors that sometimes can be considerable. A new method to calculate color coordinates and objective chromatic parameters in the color region of these olive oils is proposed with the aim of overcoming these objections. The method is a simplification of the original method proposed by the Commission Internationale de l'Eclairage (CIE), based on the measurement of the complete visible spectrum, from 380 to 770 nm. The characteristic vector analysis provides new equations to calculate tristimulus values as functions of these transmittance values based on a reconstruction of oil transmission spectra measuring from three to six wavelengths. The results show that color differences exist between the color coordinates of the experimental samples and those obtained by means of the proposed method. For more than 90% of the samples, the difference was smaller than three CIELAB units when equations based on four or more wavelengths were used.

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Virgin olive oil is extracted by mechanical means and marketed without additional processing. Olive oil color (due to chlorophyll and carotenoid compounds from the olive fruit) varies from green to yellow depending on several factors, such as olive variety, olive maturation index, oil extraction methods, and conservation conditions (1–6).

Visual estimations of oil color by comparison with material standards (colored solutions or glasses) (7,8) usually lack precision and accuracy because they are affected by the observer's subjectivity (9,10). One of the most extensively used visual comparative procedures for olive oil color is the bromthymol blue (BTB) method (11). It is based on the determination of the "BTB index," which is a color comparison of oil with a scale of nine bromthymol solutions at different pH values. A modification has been developed for virgin olive oils, suggesting a two-dimensional scale obtained by variations of pH and concentration of BTB, which uses 60 solutions as visual standards. The BTB method shows some limitations due to the subjectivity of a visual comparison, and a lack of accuracy due to the nonuniformity and instability of standards (12–14). Therefore, it can be stated that objective methods, such as trichromatic procedures, are required for color analysis of virgin olive oils.

Tristimulus colorimetry has been applied to control oil decolorations (15) and changes of color from the storage of refined oils (16). Several objective color characterizations in virgin olive oils applying trichromatic methods have been carried out. Chromatic differences between production areas, olive varieties, or fruit-ripening status have been established (2). Likewise, the influence of extraction technology has been studied, including the addition of technological adjuvants and the role of oxidative spoilage on chromatic characteristics of edible oils (17,18).

A major problem in applying tristimulus methodology is the high number of spectrophotometric measurements required to ensure a reliable calculation of tristimulus values and, from them, the rest of the chromatic parameters recommended by the Commission Internationale de l'Eclairage (CIE) (19). Olive oil industry laboratories rarely possess tristimulus colorimeters, diode array spectrophotometers, or even scanning spectrophotometers, which would provide complete visible spectra at 1-, 2-, 5-, or 10-nm intervals.

Based on a small number of transmittance measurements, diverse simplified methods to calculate tristimulus values have been proposed (20,21). These methods select, by tentative procedures, three, four, or five wavelengths, including readings around 445, 550, and 600–625 nm, and propose equations for each tristimulus value (X,Y,Z). Considerable error has been found with these methods, including in the specific color regions where the method is recommended (22,23).

A proposal for reliable simplified equations must be preceded by a validation of the reconstructed spectra obtained by specific statistical techniques. Thus, to obtain a rapid method for calculating chromatic parameters in virgin olive oils, the characteristic vector analysis (24) has been applied to reconstruct the oil transmittance spectrum from three to six transmittance measurements.

EXPERIMENTAL PROCEDURES

Samples. Samples of 1,794 virgin olive oils from diverse olive varieties (Picual, Manzanilla, Hojiblanca, Arbequina, Lechín, Verdial, Picudo) produced in Andalucía (from the

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*To whom correspondence should be addressed at Área de Nutrición y Bromatología, Facultad de Farmacia, Universidad de Sevilla, c/P. García González s/n 41012 Sevilla, Spain. E-mail: heredia@fafar.us.es south of Spain) during the harvests from 1995 to 1998 were included in the study. The oils were divided into two sets: 1200 samples (set A) were used to obtain the equations for tristimulus values, and the other 594 virgin olive oils (set B) were used as tests. Almost all the oils (1700 samples) were obtained in the laboratory by the Abencor® partial extraction method (25), reproducing the industrial procedure based on mechanical extraction with a standard, small-scale olive mill. The resulting paste was mixed in a malaxator, centrifuged at 3500 rpm, and finally decanted to obtain the oil separated from the aqueous phase. The rest of the oils (94 samples), representing large-scale production, were obtained at an industrial plant following the same process.

Apparatus. An ultraviolet/visible light diode array spectrophotometer (HP8452A; Hewlett-Packard, Palo Alto, CA) was used to obtain the spectra of the samples over the range 380–770 nm every 2 nm, employing 5-mm–pathlength cells and *n*-hexane as the reference blank.

Mathematical method. A mathematical statement of the characteristic vector analysis (26) might be given as follows: response data τ_λ (transmittance spectrum) are available for $r = 196$ 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 vectors, will adequately approximate any of the original families of response vectors. The result is that the components of the generic vectors (i.e., the transmittance spectra) can be expressed as:

$$\tau_\lambda = \overline{\tau_\lambda} + M_1 V_{1,\lambda} + M_2 V_{2,\lambda} + \cdots + MPV_{p,\lambda} \quad [1]$$

where $\overline{\tau_\lambda}$ 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.

If these expressions for τ_λ are substituted into CIE expressions for the tristimulus values, any of them, for example, X, will have the following expression:

$$X = k \sum_{\lambda=380}^{\lambda=770} (\overline{\tau_\lambda} + M_1 V_{1,\lambda} + M_2 V_{2,\lambda} + \cdots + M_p V_{p,\lambda}) L_\lambda \overline{x_\lambda} \Delta\lambda \quad [2]$$

which we can write as

$$X = k \sum_{\lambda=380}^{\lambda=770} \overline{\tau_\lambda} L_\lambda \overline{x_\lambda} \Delta\lambda + M_1 k \sum_{\lambda=380}^{\lambda=770} V_{1,\lambda} L_\lambda \overline{x_\lambda} \Delta\lambda + \cdots + M_p k \sum_{\lambda=380}^{\lambda=770} V_{p,\lambda} L_\lambda \overline{x_\lambda} \Delta\lambda \quad [3]$$

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

Calling

$$X_i = k \sum_{\lambda=380}^{\lambda=770} V_{i,\lambda} L_\lambda \overline{x_\lambda} \Delta\lambda \quad [4]$$

we can write Equation 3 as

$$X = X_0 + M_1 X_1 + M_2 X_2 + \cdots + M_p X_p \quad [5]$$

where X_0 is the tristimulus value corresponding to the mean transmittance spectrum and the 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 Equation 1 must be measured, and the following system of equations must be solved:

$$\begin{array}{l} \tau_{\lambda 1} = \overline{\tau_{\lambda 1}} + M_1 V_{1,\lambda 1} + M_2 V_{2,\lambda 1} + \cdots + MPV_{p,\lambda 1} \\ \tau_{\lambda 2} = \overline{\tau_{\lambda 2}} + M_1 V_{1,\lambda 2} + M_2 V_{2,\lambda 2} + \cdots + MPV_{p,\lambda 2} \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ \tau_{\lambda p} = \overline{\tau_{\lambda p}} + M_1 V_{1,\lambda p} + M_2 V_{2,\lambda p} + \cdots + MPV_{p,\lambda p} \end{array} \quad [6]$$

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

Since the M_i coefficients calculated from Equation 6 are functions of the measured transmittances, $\tau_{\lambda i}$, they can be substituted into Equation 5, giving

$$X = C_{0X} + C_{1X}\tau_{\lambda 1} + C_{2X}\tau_{\lambda 2} + \cdots + C_{pX}\tau_{\lambda p} \quad [7]$$

By analogous argument for Y and Z, we may write

$$\begin{array}{l} Y = C_{0Y} + C_{1Y}\tau_{\lambda 1} + C_{2Y}\tau_{\lambda 2} + \cdots + C_{pY}\tau_{\lambda p} \\ Z = C_{0Z} + C_{1Z}\tau_{\lambda 1} + C_{2Z}\tau_{\lambda 2} + \cdots + C_{pZ}\tau_{\lambda p} \end{array} \quad [8]$$

that express the tristimulus values directly as a function of the measured transmittance. 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 an adaptation of the method by Simonds (24), using our own software.

After calculating the first six characteristic vectors, and in view of the high percentage of the variability of data explained by them, six reconstructions of each spectrum were carried out using the mathematical method. This method starts with the mean vector and the first characteristic vector and then adds the corresponding characteristic vector, to each following reconstruction, multiplying each vector V_i by its M_i coefficient.

Based on the experimental and reconstituted spectra, the color coordinates were calculated using the CIE 1964 standard observer and the illuminant D65, following CIE recommendations (21).

Theoretically, any set of p wavelengths could be used to obtain the transmittances $\tau_{\lambda i}$ in Equations 7 and 8, 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.

Using the coordinates obtained on applying the CIE method to the experimental spectra as reference coordinates, color differences were calculated. The calculation was measured in CIELAB units, between these coordinates and those obtained from the reconstructed spectra as well as those calculated from tristimulus values obtained using Equations 7 and 8.

RESULTS AND DISCUSSION

Figure 1 shows the mean vector and the six characteristic vectors obtained in the process for the 1200 olive oils (set A). The spectra of three olive oil samples, experimentally measured and reconstituted with three characteristic vectors, are shown in Figure 2 as an example. After analyzing these results, we concluded that the reconstruction of spectra obtained from three characteristic vectors was satisfactory, since the color differences were lower than three CIELAB units for 924 samples (77.00%). After calculating the tristimulus values corresponding to the mean vector and the first three characteristic vectors and substituting them into Equation 5, the following expressions were obtained for the tristimulus values of any olive oil sample:

$$\begin{aligned} X &= 73.262 + 247.996M_1 + 107.107M_2 + 21.908M_3 \\ Y &= 79.043 + 261.915M_1 + 120.942M_2 + 31.819M_3 \\ Z &= 31.741 + 647.353M_1 - 128.857M_2 + 55.065M_3 \end{aligned} \qquad [9]$$

To obtain the best results using Equation 7, we searched for wavelength triads using scans around 450, 550, and 600 nm, because in previous work the best results were obtained in these areas of the spectrum (27,28). The wavelengths selected were 430, 482, and 600 nm and Equation 6 became:

$$\begin{aligned} \tau_{430} &= 0.264 + 6.091M_1 - 1.095M_2 + 0.215M_3 \\ \tau_{482} &= 0.313 + 6.127M_1 - 1.433M_2 + 0.824M_3 \\ \tau_{600} &= 0.901 + 1.624M_1 + 1.691M_2 + 0.234M_3 \end{aligned} \qquad [10]$$

where τ_{430}, τ_{482}; and τ_{600} are the transmittances measured at these wavelengths. Solving for M_1, M_2, and M_3 in Equation 10 and substituting into Equation 9, we find the following expressions for tristimulus values:

$$\begin{aligned} X &= 20.885\tau_{430} - 0.541\tau_{482} + 76.422\tau_{600} - 0.931 \\ Y &= 7.838\tau_{430} + 11.963\tau_{482} + 86.751\tau_{600} - 4.920 \\ Z &= 52.961\tau_{430} + 52.347\tau_{482} + 2.463\tau_{600} - 0.824 \end{aligned} \qquad [11]$$

After calculating the tristimulus values of the 1200 olive oil samples from Equation 11, their CIELAB color coordinates and the corresponding color differences with respect to the reference color coordinates were obtained. These color differences were lower than three CIELAB units for 91.16% of the samples, which improves on the previous result. To confirm the usefulness of this method, the expressions were applied to 594 olive oil samples (set B) that were not used in the calculation method. In this case, color differences lower than three CIELAB units reached 89.73%.

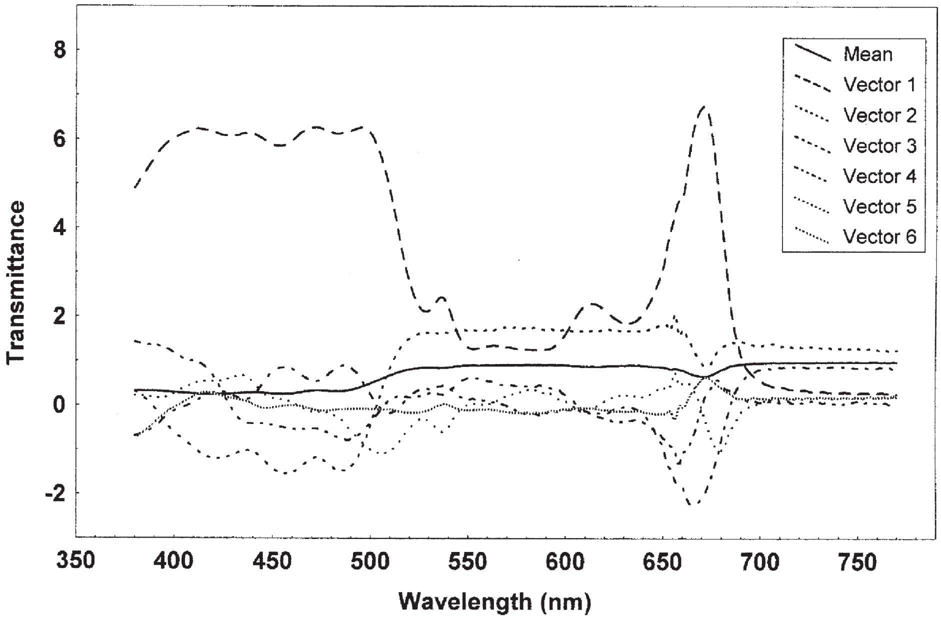

FIG. 1. Mean vector and the first six characteristic vectors obtained for the 1200 olive oils (set A).

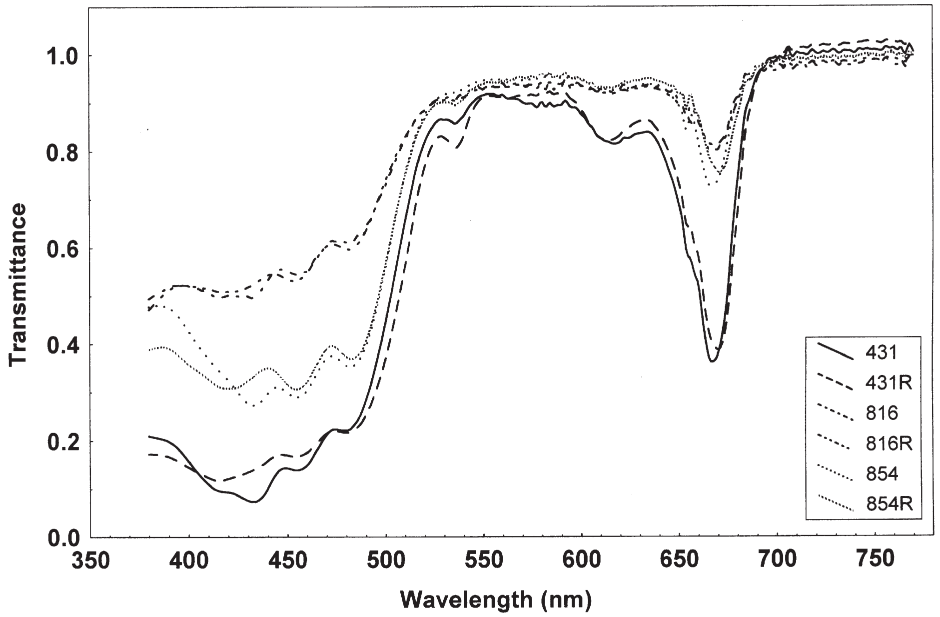

FIG. 2. Comparison of the reflectance spectra, experimentally measured and reconstituted (R) with three characteristic vectors of three representative virgin olive oils.

To improve this result, the entire process was repeated, increasing the number of characteristic vectors. The expressions obtained for four vectors were

$$\begin{aligned} X &= -4.303\tau_{396} + 18.335\tau_{446} + 43.829\tau_{526} + 33.408\tau_{622} + 2.741 \\ Y &= -4.566\tau_{396} + 17.569\tau_{446} + 66.466\tau_{526} + 19.458\tau_{622} + 2.133 \\ Z &= 6.893\tau_{396} + 101.168\tau_{446} - 0.838\tau_{526} + 1.750\tau_{622} + 0.700 \end{aligned} \qquad [12]$$

Color differences of less than three units are now included in 94.78% of test samples. When characteristic vectors were increased to five, the expressions for tristimulus values were

$$\begin{aligned} X &= 5.393\tau_{424} + 12.141\tau_{446} + 15.444\tau_{520} + 27.067\tau_{570} + 34.358\tau_{628} + 0.725 \\ Y &= -5.811\tau_{424} + 18.709\tau_{446} + 47.770\tau_{520} + 29.738\tau_{570} + 7.979\tau_{628} + 2.581 \\ Z &= 8.423\tau_{424} + 95.562\tau_{446} + 14.538\tau_{520} - 10.715\tau_{570} - 0.773\tau_{628} + 1.780 \end{aligned} \qquad [13]$$

In this case, 97.64% of color differences were less than three units. When the number of vectors was raised to six, the expressions were

$$\begin{aligned} X &= 4.490\tau_{380} - 5.828\tau_{388} + 21.901\tau_{440} - 1.498\tau_{460} + 11.177\tau_{522} + 64.518\tau_{600} + 0.465 \\ Y &= -1.286\tau_{380} - 1.694\tau_{388} + 8.396\tau_{440} + 6.622\tau_{460} + 52.338\tau_{522} + 34.672\tau_{600} + 1.475 \\ Z &= -17.850\tau_{380} + 25.616\tau_{388} + 37.867\tau_{440} + 58.136\tau_{460} + 12.548\tau_{522} - 9.923\tau_{600} + 1.270 \end{aligned} \qquad [14]$$

The percentage of color differences lower than three now reached 98.15%, which we consider satisfactory, as addition of further vectors added excessive complication when compared with the small improvement obtained.

Figure 3 shows the results obtained when three, four, five or six vectors were applied to the reconstruction of the spectra. Color differences, obtained between experimentally measured and reconstituted spectra, demonstrated that only for a

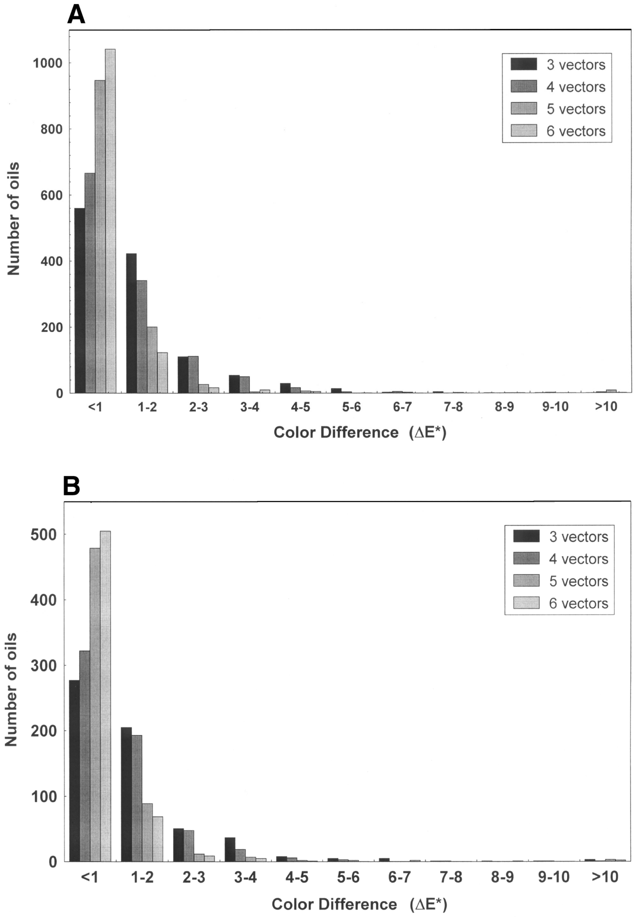

FIG. 3. Frequency histogram of color differences for 3, 4, 5, and 6 measurements. (A) Set A (1200 oils); (B) set B (594 test oils).

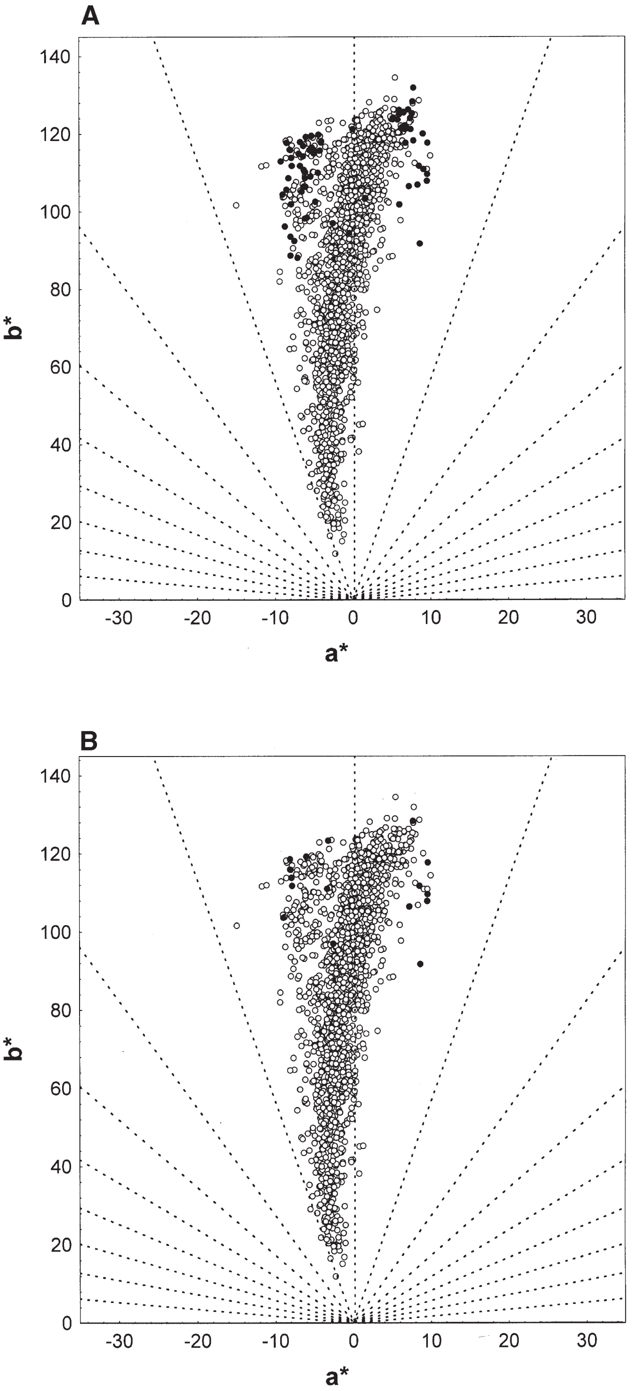

FIG. 4. Representation of the olive oils on the CIELAB chromaticity (a*b*)-diagram: ○, oils with spectrum reconstruction with $\Delta E < 3$ CIELAB units; ●, oils with spectrum reconstruction with $\Delta E > 3$ CIELAB units. (A) four vectors; (B) six vectors.

small percentage of samples (in sets A and B) the reconstruction of their spectra not possible with sufficient reliability, especially with the use of five- or six-wavelength data. Figure 4 shows the location of the samples on the (a*b*)-chromaticity diagram (by CIELAB space), indicating those olive oils with poorly reconstructed spectra (color differences >3 units). As can be seen, this occurred for several oils with high chroma values (distance to coordinate origin). This means the colors of the samples were visually intense (e.g., oxidized olive oils).

The characteristic vector analysis was applicable to the reconstruction of olive oil sample transmittance spectra, and the use of a few of them was sufficient for close approximation when the spectrophotometric measurements were made with 0.5-cm–pathlength cells. Equations 11 and 12, on a basis of three and four vectors, respectively, gave similar results and could be routinely used satisfactorily, with the limitation mentioned. Equations 13 and 14, for five and six vectors, respectively, gave the better results for the spectra reconstruction.

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