Measurement of the concentrations of solutions through chromatic systems

D. Escolar, M. R. Haro, A. Saucedo, J. Ayuso, A. Jiménez, and J. A. Alvarez

After a careful check of the response linearity of the spectrophotometer in absorbances and transmittances at wavelengths between 250 and 550 nm with potassium dichromate, the influence of the concentration of solutions on the tristimulus coordinates and the coordinates of the CIE 1931 (Commission Internationale de l'Éclairage) and CIELAB colorimetric systems was analyzed. How to use the value of only some chromatic coordinates to obtain a sample's concentration simultaneously is also shown.

1. Introduction

By means of the absorbance values of a solution's components at a certain wavelength its concentration can be obtained relatively quickly thanks to the linear relationship between absorbance and concentration according to the Lambert–Beer law. However, even when the solutions are diluted certain deviations of the law occur, mainly because the incident beam is not monochromatic because of scattered radiation and a finite slit width. Hence, for certain cases it would be better to characterize the absorption intensity not by its value at the maximum of a band but rather by the band area. The integration should be performed from $-\infty$ to $+\infty$, but in practice the limits are fixed at the beginning of the neighboring bands. The same can be argued for any spectral band, and thus the entire area under the spectral profile can be considered to be proportional to the sample's concentration. Because modern spectrophotometers are controlled by computer, the calculation of the area does not pose any particular problem.

On the other hand, for chromatic-parameter determinations to be reliable[1] the transmittance measurements have to be taken along the entire visible interval. Moreover, as this implies the measurement of the area under the spectral profile, it is of interest to establish the relation that might exist between chromatic parameters and the concentration of a solution, which could result in an additional, useful value—apart from the colorimetric data by spectrophotometry—such as the concentration of a solution.

Because of their extensive use by various authors, the chromatic-representation systems CIE 1931[2–5] and CIELAB 1976[2,6,7] deserve special attention because of their uniformity.[8–11] A bibliographical search did not come up with any relations between a solution's concentration and the parameters of the CIE 1931 chromatic system, although we did find a relation of the polynomial type between some chromatic parameters of the CIELAB system and the concentration.[9] For this reason the behavior of the chromatic parameters of the CIE 1931 and the CIELAB system has been studied [see Eqs. (A1)–(A6) in Appendix A] through variation of a solution's concentration. For this study we chose potassium dichromate solutions because no other chemical equilibriums occur within the studied concentration range that might distort the results except for the ionic dissociation. We also chose this compound because it is the recommended standard for the calibration of UV/V spectrophotometers.[12]

2. Materials and Methods

To prepare the 10 potassium dichromate solutions in sulfuric acid (5.0×10^{-3} M) with concentrations from 7.43×10^{-5} M to 6.80×10^{-4} M, we used products from Merck. First the solution with the highest concentration was prepared by dissolution of 0.2 g of potassium dichromate in sulfuric acid until 1 L was obtained, from which the other solutions were prepared.

The spectra of the solutions were recorded in the visible zone with a Perkin-Elmer Lambda 5 spectro-

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The authors are with the Departamento Quimica Fisica, Universidad Cadiz, Apartado 40, E-11510 Puerto Real, Cadiz, Spain.

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photometer equipped with an interface processor that permitted digitization of the data at an interval of up to 0.1 nm. The optical system was equivalent to a C illuminant with a foveal angle of less than 4°. The slit width was 1 nm (the appropriate width for the absorption bands studied); thus it provided a favorable signal-to-noise ratio. Samples were measured in a 1-cm lightpath thermostatted cell, and the temperature was maintained at 25 °C.

For the calculation of the tristimulus coordinates measurements were sometimes taken at only four wavelengths, and sometimes at 16. Although a calculation that uses 39 measurements from 380 to 770 nm is considered adequate, we have, however, taken 391 measurements at 1-nm intervals, because a sum of small intervals better approximates the integral that is required for the calculation of the chromatic coordinates.[1,2] The calculations have been carried out with a computer program developed in our laboratory that gives us the tristimulus values and the chomatic parameters in the various colorimetric systems.

3. Results and Discussion

We first checked whether the potassium dichromate solutions obeyed the Lambert–Beer law in our experimental system by examining both the relation between the absorbance and the concentration at the wavelength of the absorption maxima and the relation between the area below the entire spectral profile and the concentration.

Figure 1 shows the well-known spectra of potassium dichromate in an acid solution, for which we used a solution of sulfuric acid in the reference cell. No displacement of the band maxima is observed with variation of the concentration, and the absorbance is practically zero above 539 nm. The natural bandwidth was 62 nm at 350 nm, which is more than 10 times the spectral bandwidth. To examine the relation between the area below the spectral profile and the concentration, the recordings were prolonged outside the visible region—from 250 to 770 nm—while a check of whether the band area was affected by the cutoff in the profile at 200 nm was made.

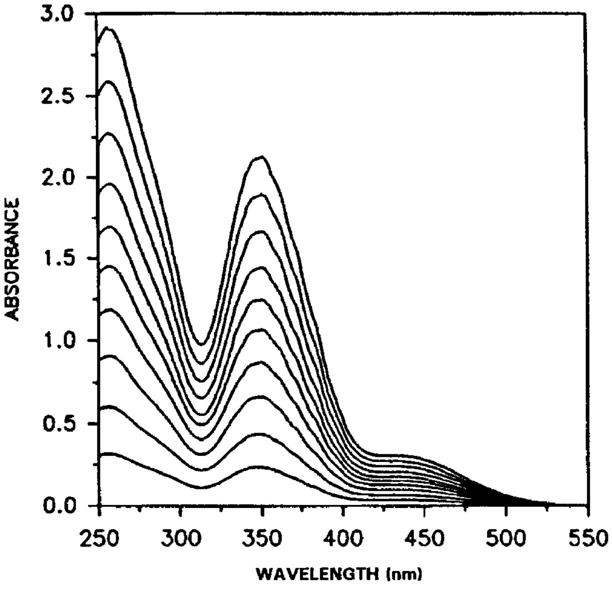

Fig. 1. Absorption spectra of potassium dichromate [(7.43 at 68.0) × 10^{-5} M] in sulfuric acid solutions (5.0 × 10^{-3} M).

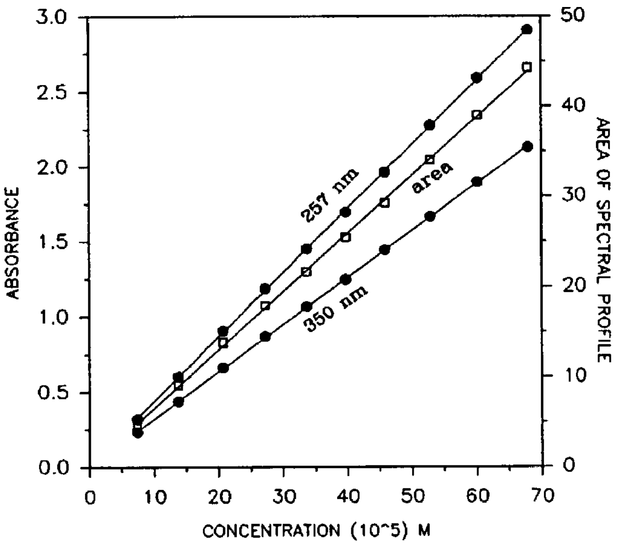

Fig. 2. Absorbance versus concentration for potassium dichromate in sulfuric acid solutions, and the area under the spectral profile (250–550 nm) versus concentration.

In Fig. 2 one can observe how well the Lambert–Beer law is obeyed at the wavelengths of the absorption maximum. The regression lines are $A_{257}^{\max} = (1.2 \pm 0.7) \times 10^{-2} + (42.7 \pm 0.2) \times 10^{2} c$ with $r = 0.999$ and $A_{350}^{\max} = (0.8 \pm 0.4) \times 10^{-2} + (31.3 \pm 0.1) \times 10^{2} c$ with $r = 0.999$; the intercept and the slope are given with their standard error. In both cases the intercept is near, but not equal to, zero because of small errors in the absorbance values.

The above results are usual and well known. However, what is not usually mentioned nor so well known is that, in solutions of the types that yield the above spectra, the Lambert–Beer law is obeyed at any wavelength, but not necessarily at the maxima of the bands. To verify this, we measured the absorbance at every nanometer in every spectrum that fits all the lines like those shown in Fig. 2, but we measured the absorbance at every nanometer for the various concentrations in the interval 250–550 nm (the visible interval was elongated into the ultraviolet for reasons of verification). The results confirm that the Lambert–Beer law is obeyed at any selected wavelength in the visible and ultraviolet regions, and only above 530 nm is $r < 0.999$, because the absorbance becomes practically equal to the noise.

In Fig. 2, the areas under the spectral profile are also represented by empty squares. This area has been calculated as $\Sigma\, [(A_\lambda)(\Delta\lambda)]$, or the sum of the areas resulting from the product of absorbance, A_λ, by the wavelength interval between two consecutive values, $\Delta\lambda$. The total area of the spectral profile varies linearly with the concentration when $\Delta\lambda = 1$ nm, and the regression line is area = $(7 \pm 19) \times 10^{-2} + (645 \pm 5) \times 10^{2}c$ with $r = 0.999$. The visible absorption interval 380–550 nm, which is the one that is of interest for the calculation of the chromatic parameters, falls within the examined spectral zone, 250–580 nm.

Because the chromatic coordinates are obtained from the transmittance values (which are usually obtained by transformation of the absorbance values), we have carried out an analysis similar to the one mentioned above but using the spectral-transmittance values. As was to be expected, the linear correlation coefficients are as good as before the use of logarithmic fitting.

The above verification of the spectrophotometer should be performed prior to the study of the dependence of the chromatic coordinates with the concentration because we then have disposed of a set of spectral data (absorption and area) that varies linearly with the concentration. One should bear in mind, however, that better chromatic-parameter values are obtained when the calculations are based on a large number of values over the entire visible absorption interval; hence it is advisable to verify the above linearities at any wavelength.

A. Variation of the Tristimulus Values with the Concentration

Given that for the calculation of the tristimulus values it is necessary to transform the absorbances into transmittances and that there exists an exponential relation between both, one can also expect logarithmic behavior in the relation between the tristimulus values and the concentration, or linear behavior that would correspond with the first terms of the expansion of the exponential function, which is valid for small concentrations.

Through a computer program, the tristimulus values of the different concentrations have been obtained, and the results are shown in Fig. 3. The values of X, Y, and Z diminish with an increasing concentration, although the variation is much bigger for Z; for the three cases the behavior is approximately linear. The Y coordinate does not vary significantly with the concentration; the X coordinate shows a more pronounced variation and the Z coordinate is the most affected by the change in concentration.

The above data have been fitted to linear and logarithmic regressions, and X and Z yield good linear correlation coefficients, as is shown in Table 1. An even better correlation coefficient results from the logarithmic regression, with $r = -0.999$ and the equation $\log Z = 6.77 \times 10^{-2} - 342.0c$. This indicates that the variation of Z with the concentration is better approximated by means of an exponential function instead of a linear one.

B. Color Evaluation in the Chromatic Diagrams

We now examine how variation of the tristimulus coordinates with the concentration affects the chromaticity diagrams and the chromatic parameters of the CIE 1931 and CIELAB 1976 systems.

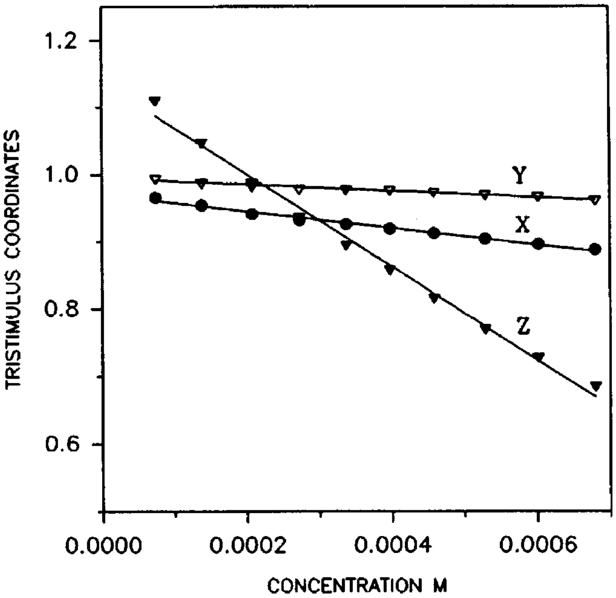

Fig. 3. Variation of the tristimulus coordinates with the concentration of potassium dichromate in sulfuric acid solutions.

1. *Changes in the CIE 1931 Diagram*

The CIE 1931 chromaticity diagram shown in Fig. 4 represents the two-dimensional chromaticity coordinates calculated from the tristimulus coordinates. The x and y coordinates increase with the concentration of the potassium dichromate solution and are represented by the points $A_i(x_i, y_i)$. An increase in the concentration displaces points A_i toward positions with higher saturation in the yellow zone. In general, the variation in concentration produces a line whose origin is the CIE standard illuminant C.

Fitting points A_i to a line yields $r = 0.999$. This linear behavior is due to the specific characteristics of the solutions used, and it is to be expected that other solutions that do not follow the Lambert–Beer law to the same degree in the spectral interval would yield curves. Hence, in general, when the concentration is increased points $A_i(x_i, y_i)$ form part of a curve with the origin at O (illuminant coordinates) in Fig. 4, which would intercept the chromaticity diagram at the dominant wavelength, point B in the figure. An increase in the concentration does not produce substantial changes in the dominant wavelength for solutions that obey the Lambert–Beer law, as can be seen from Table 2. When the curve becomes a

Table 1. Linear Least-Squares Fits of the Tristimulus Coordinates against the Concentration of Potassium Dichromate in Sulfuric Acid Solutions

Tristimulus Coordinate	Equations	r
X	$(970 \pm 2) \times 10^{-3} - (124 \pm 5)c$	−0.994
Y	$(994 \pm 1) \times 10^{-3} - (47 \pm 3)c$	−0.986
Z	$(1139 \pm 9) \times 10^{-3} - (691 \pm 21)c$	−0.996

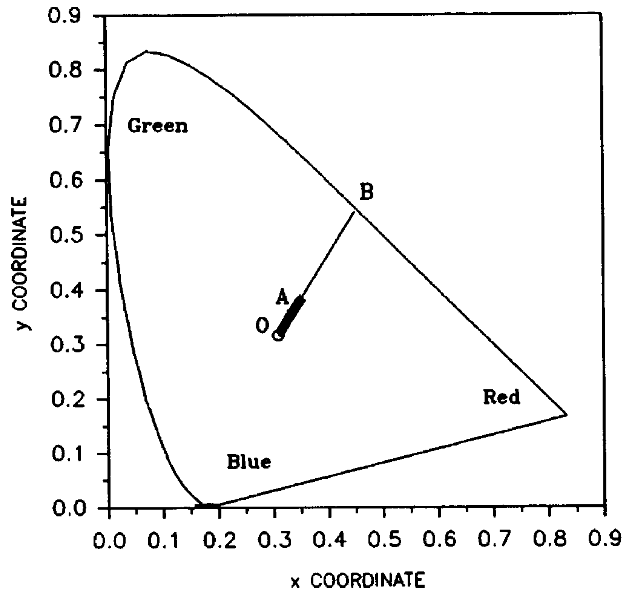

Fig. 4. CIE 1931 chromaticity diagram showing the colors of potassium dichromate in sulfuric acid solutions.

straight line, the dominant wavelength (in this case at 571.3 nm) is the average of the data shown in Table 2.

The luminosity L of the solutions varies with the concentration in the same manner as the tristimulus coordinate Y, discussed above. The saturation S increases with the concentration because the length of segment OA increases. In this case S is fitted with equal linear excellence, as can be observed from Table 3.

2. *Change of Color in the CIELAB Chromatic Space*

In Table 4 are shown the chromatic parameters of the CIELAB system obtained from the tristimulus values. The lightness L^* diminishes with increasing concentration; at the same time there is an increase in the chroma C^* as a consequence of the way in which the coordinates a^* and b^* vary. The tendency of the hue H^* is to remain constant, as did the dominant wavelength in the CIE 1931 system. This constancy is confirmed when b^* is represented against a^*, and the linear relation $b^* = -1.18 - 3.10a^*$ is thereby obtained with a correlation coefficient of $r = 0.997$.

Table 3. Linear Equations that Relate the Chromatic Parameters of the CIE 1931 and CIELAB Systems with the Concentration for Potassium Dichromate Solutions

System	Equations	r
CIE 1931		
Luminosity L	$(99.45 \pm 0.13) - (4660 \pm 31)c$	0.983
Saturation S	$(0.68 \pm 0.17) - (4017 \pm 404)c$	0.999
CIELAB 1976		
a^*	$-(72 \pm 2) \times 10^{-2} - (14194 \pm 536)c$	0.994
b^*	$(92 \pm 2) \times 10^{-2} + (44357 \pm 544)c$	0.999
Lightness L^*	$(99.79 \pm 0.01) - (1835 \pm 121)c$	0.983
Chroma C^*	$(1.11 \pm 0.03) - (46568 \pm 663)c$	0.999
Hue H^*	$(110.73 \pm 0.03) - (3798 \pm 717)c$	0.882
Color difference ΔE^*	$(1.12 \pm 0.03) + (46600 \pm 664)c$	0.999

Applying this linear relation to Eq. (A4) results in $H^* = \arctan(-1.18/a^* - 3.10)$ depending on the coordinate a^*. Because the experimental data for the coordinate a^* increase in absolute terms with the concentration, the term $-1.18/a^*$ decreases and therefore contributes to a lesser extent to the value of H^*, which thus depends only on the constant term. As a result the hue value can be approximated by the average value of those tabulated. For solutions of inorganic salts of copper (II) and cobalt (II), the bibliography shows that the hue and the concentration fit linearly, as has also been found in this research.[9]

Figure 5 shows the behavior of a^* and b^* with the concentration. The linear fit of coordinate a^*, although a good one, can be improved by logarithmic fitting. Coordinate b^*, chroma c^*, and color difference ΔE yield good linear correlations. Lightness L^* and hue H^* do not yield equally good linear correlations, and no better fittings result from exponential functions.

Figure 6 shows the good linear dependence between the color differences of the solutions and the concentrations, even though the lightness that takes part in the calculation of the color difference ΔE^* fits less linearly than do a^* and b^*, which also intervene in the calculation of ΔE^*. Thus a variation in the concentration leads to a proportional variation in the color difference between two solutions. This linear behavior of ΔE^* with the concentration is due to the

Table 2. Variation of the Coordinates of the CIE 1931 System with the Concentration of Potassium Dichromate

c (10^4 M)	x	y	L	λ_{dom}	S
0.743	0.315	0.324	99.43	571.1	3.23
1.379	0.319	0.330	98.77	571.4	6.16
2.074	0.323	0.337	98.25	571.4	9.19
2.726	0.327	0.344	97.90	571.4	11.92
3.370	0.331	0.350	97.84	571.3	14.44
3.974	0.334	0.355	97.73	571.0	16.58
4.582	0.337	0.361	97.41	571.3	19.19
5.286	0.342	0.367	97.03	571.4	22.01
6.017	0.346	0.373	96.74	571.4	24.81
6.798	0.350	0.380	96.22	571.5	27.69

Table 4. Variation with the Concentration of Potassium Dichromate of the CIELAB 1976 Coordinates

c (10^{-4} M)	a^*	b^*	L^*	C^*	H^*
0.743	−1.38	3.64	99.78	3.89	110.76
1.379	−2.49	6.93	99.52	7.37	109.74
2.074	−3.71	10.33	99.32	10.98	109.71
2.726	−4.71	13.36	99.18	14.17	109.39
3.370	−5.73	16.18	99.16	17.16	109.46
3.974	−6.84	18.61	99.12	19.82	110.15
4.582	−7.45	21.42	98.99	22.68	109.14
5.286	−8.32	24.49	98.84	25.87	108.74
6.017	−9.18	27.54	98.72	29.04	108.40
6.798	−9.84	30.63	98.52	32.17	107.78

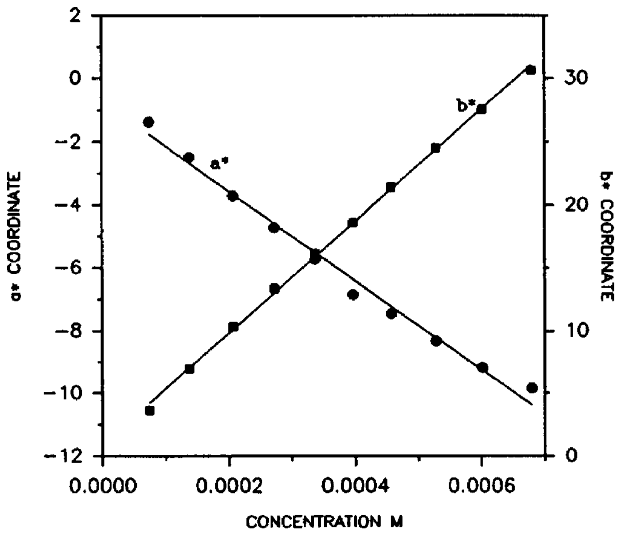

Fig. 5. Variation of the coordinates a^* and b^* with the concentration of potassium dichromate in sulfuric acid solutions.

uniformity of the CIELAB color representation system, and it is therefore the most adequate for color measurements and color differences between solutions. The fitting results for each of the coordinates of this system are shown in Table 3.

4. Conclusions

From the above it can be concluded that, apart from the color characterization, the CIELAB system will yield the concentration of a solution quickly and easily through the use of the calibration line for a chromatic parameter, as in other methods. This calibration line can be established between the concentration and any of the chromatic parameters x and y, or the saturation S of the CIE 1931 system, as well as the parameters a^*, b^*, chroma C^*, and color difference ΔE^* of the CIELAB system. There exist colorimeters and spectrophotometers that directly give the values of the chromatic coordinates in those colorimetric systems (usually a^*, b^*, and L^*) and hence could also supply the concentration. Even so and despite the good results shown above, it would be advisable to continue to work on other cases, mainly for solutions that do not follow the Lambert–Beer law well, e.g., multicomponent solutions and solids.

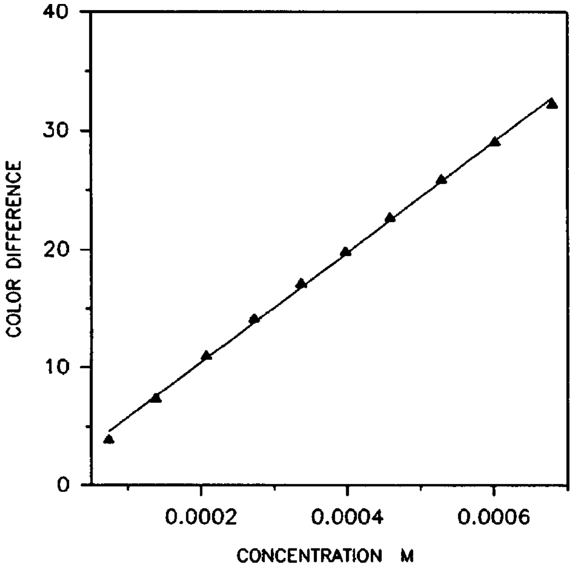

Fig. 6. Color difference versus the concentration of potassium dichromate in sulfuric acid solutions.

Appendix A.

From the tristimulus values, the chromaticity coordinates of the CIE 1931 system are calculated from $x = X/(X + Y + Z)$ and $y = Y/(X + Y + Z)$. The Y tristimulus represents the parameter luminosity L; dominant wavelengths λ_{dom} and saturation (or purity) S are the other representative chromatic parameters of this system. The dominant wavelength of a color stimulus is the wavelength of the monochromatic stimulus that, when additively mixed in suitable proportions with a specified achromatic stimulus, yields a color match with the color stimulus considered. Saturation of a color stimulus is the ratio of two lengths on a chromaticity diagram. The first length is the distance between the point representing the chromaticity of a specified achromatic stimulus and that representing the chromaticity of the color stimulus considered. The second length is the distance along the same direction and from the first point to the edge of the chromaticity diagram.^{2}

In the CIELAB system the space in the shape of a semi-ellipsoid is transformed into a space of cylindrical coordinates that result from the CIE 1931 system. The equations for the transformation of the tristimulus X, Y, and Z values to the coordinate values L^*, a^*, and b^* of the CIELAB are

$$a^* = 500[f(X/X_0) - f(Y/Y_0)], \tag{A1}$$

$$b^* = 200[f(Y/Y_0) - f(Z/Z_0)], \tag{A2}$$

with

$$f(q) = \begin{cases} (q)^{1/3} & q > 0.008856 \\ 7.787q + \dfrac{16}{116} & q \leq 0.008856 \end{cases}, \tag{A3}$$

$$L^* = \begin{cases} 116(Y/Y_0)^{1/3} - 16 & Y/Y_0 > 0.008856 \\ 903.3(Y/Y_0) & Y/Y_0 \leq 0.008856 \end{cases}, \tag{A4}$$

where X_0, Y_0, and Z_0 represent the tristimulus values corresponding to the achromatic stimulus used and depending on the standardized illuminant in the chosen chromatic space.

Together with lightness L^*, the chromatic parameters hue H^* and chroma C^* are defined, and they result from the transformation of the Cartesian coordinates a^* and b^* to polar coordinates. The hue determines the color of a substance on a chromatic circle with a scale of 0° to 360°, and chroma determines the color intensity defined by the hue parameter. The definitions for hue and chroma are

$$H^* = \arctan\left(\frac{\nu}{a^*}\right), \tag{A5}$$

$$C^* = [(a^*)^2 + (b^*)^2]^{1/2}. \tag{A6}$$

The color differences are measured with

$$\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}. \tag{A7}$$

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