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Analytical colorimetry —

Part 2:
Saunderson correction, solutions of the Kubelka-Munk equation, tinting strength, hiding power

Analyse colorimétrique —

Partie 2: Correction de Saunderson, solutions de l'équation de Kubelka-Munk, force colorante, pouvoir couvrant

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Contents

Foreword

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The committee responsible for this document is ISO/TC 256, *Pigments, dyestuffs and fillers*.

ISO 18314 consists of the following parts, under the general title *Analytical colorimetry*:

- — *Part 1: Practical colour measurement*
- — *Part 2: Saunderson correction, solutions of the Kubelka-Munk equation, tinting strength, hiding power*
- — *Part 3: Special indices*

Analytical colorimetry —

Part 2:
Saunderson correction, solutions of the Kubelka-Munk equation, tinting strength, hiding power

1 Scope

This part of ISO 18314 specifies the Saunderson correction for different measurement geometries and the solutions of the Kubelka-Munk equation for hiding and transparent layers. It also specifies methods for the calculations of the tinting strength including the residual colour difference with different criteria and of the hiding power.

The procedures for preparing the samples for these measurements are not part of this part of ISO 18314. They are agreed between the contracting parties or are described in other national or International Standards.

2 Terms, definitions, symbols, and abbreviated terms

2.1 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

2.1.1
tinting strength
measure of the ability of a colorant, based on its absorption, to impart colour to other materials

2.1.2
relative tinting strength
C_{rel}
percentage ratio of those mass fractions of the coloured pigment reference and test samples (m_r and m_t, respectively) that cause the particular tinting strength criterion used to have identical values for the reference and test samples

2.1.3
tinting strength criterion
parameter that describes the colouring effect of a colorant, based on its absorption

Note 1 to entry: The tinting strength criteria used in this part of ISO 18314 are the following:

- value of the Kubelka-Munk function at the absorption maximum;
- weighted sum of the Kubelka-Munk function values;
- tristimulus value Y;
- the smallest of the tristimulus values X, Y, Z;
- shade depth parameter B.

Examples of other tinting strength parameters not used in this part of ISO 18314 are the following:

- unweighted sum of the Kubelka-Munk function values;
- chromaticity given by the three colour coordinates (L*, a*, b*);

— reflectance factor at the absorption maximum.

2.1.4

residual colour difference

colour difference that remains between the white reductions of the reference and test samples when the tinting strength criterion values are the same or have been equalized

EXAMPLE Given by ΔE^*.

2.1.5

standard shade depth

shade depth

measure of the intensity of a colour sensation, which increases with increasing chroma and decreases with increasing lightness

Note 1 to entry: Standard shade depths are values set by convention. For colourimetric purposes, the standard shade depth is defined by the shade depth parameter B = 0, which is calculated from the tristimulus value, Y, and the chromaticity coordinates, x and y.

2.1.6

hiding power

ability of a pigmented medium to hide the colour or the colour differences of a substrate

2.2 Symbols and abbreviated terms

a	constant
α^*	CIELAB colour coordinate
$a(\varphi)$	factor
$a(\lambda)$	auxiliary variable
b^*	CIELAB colour coordinate
$b(\lambda)$	auxiliary variable
B	shade depth parameter
C_{rel}	relative tinting strength
D_{m}	hiding power value indicating the area of the contrast substrate concerned, in m^2, which can be coated with 1 kg
D_{v}	hiding power value indicating the area of the contrast substrate concerned, in m^2, which can be coated with 1 l
$F(\lambda)$	Kubelka-Munk function
$F'(\lambda)$	modified Kubelka-Munk function
$g(\lambda)$	weighting function (defined as the sum of the colour matching functions $\bar{x}(\lambda)$, $\bar{y}(\lambda)$, and $\bar{z}(\lambda)$ for a 10° standard observer)
h	thickness
K	coefficient

$K(\lambda)$	absorption coefficient
$(K/S)_\mathrm{r}$	Kubelka-Munk value of reference sample
$(K/S)_\mathrm{t}$	Kubelka-Munk value of test sample
L^*	CIELAB lightness
m_r	mass fraction of coloured pigment reference sample
m_t	mass fraction of coloured pigment test sample
n	refractive index
r_0	reflection coefficient at the surface for directional light incident perpendicular from outside
$\overline{r}_0$	reflection coefficient at the surface for directional light incident parallel under 45° from outside
r_2	reflection coefficient for light incident diffusely from the inside of the specimen
$R(\lambda)$	reflectance spectrum
$R(\lambda)_\infty$	reflectance of infinitely thick layer
$R(\lambda)^*$	reflectance of the sample
$R(\lambda)^*_\mathrm{ob}$	Saunderson-corrected reflectance of the black substrate
$R(\lambda)^*_\mathrm{ow}$	Saunderson-corrected reflectance of the white substrate
$R(\lambda)^*_\mathrm{b}$	Saunderson-corrected reflectance of the sample on black substrate
$R(\lambda)^*_\mathrm{w}$	Saunderson-corrected reflectance of the sample on white substrate
$R'(\lambda)$	modified reflectance spectrum including surface effects
s	saturation
$S(\lambda)$	scattering coefficient
T	weighted sum
x, y	chromaticity coordinates
X, Y, Z	tristimulus values
ΔE^*	residual colour difference

ΔE^*_{ab}	CIELAB colour difference
φ	hue angle
φ_0	closest angle in the table below the hue angle

3 Saunderson correction

3.1 General

For colourimetric calculation it is necessary to account for surface phenomena to obtain viable results. The formulas are known as Saunderson correction, their derivation can be found in References [1] and [2] The necessary coefficients are solutions of the Fresnel formulae[3] depending on the index of refraction for the given binder.

The formulae are derived assuming an ideal surface, a perfectly hiding layer and a perfectly diffuse scattering of light inside the interior of the specimen. Any deviation from these assumptions shall lead to consideration of the usefulness of the following calculations.

The formulae given here are for two of the most widespread geometries: diffuse incidence, 0° observation (d/0°) and 45° incidence, 0° observation (45°/0°). In nearly every colourimeter used, the measurement angle is not 0° but 8°. This deviation is not considered problematic.

The constants necessary for the calculation are the following:

r_0:	reflection coefficient at the surface for directional light incident perpendicular from outside. For $n = 1{,}5$ $r_0 = 0{,}040$.
$\overline{r}_0$:	reflection coefficient at the surface for directional light incident parallel under 45° from outside. For $n = 1{,}5$, $r_0 = 0{,}050$.
r_2:	reflection coefficient for light incident diffusely from the inside of the specimen. For $n = 1{,}5$, $r_2 = 0{,}596$.

3.2 Incidence diffuse, observation 0° (d/0°)

The constant a = 1 if a gloss trap is closed and a = 0 if the gloss trap is open and the specular reflection is excluded.

$$R(\lambda) = ar_0 + \frac{(1-r_0)(1-r_2)R(\lambda)^*}{1-r_2R(\lambda)^*} \quad (1)$$

$$\text{for a} = 1: \quad R(\lambda)^* = \frac{R(\lambda)-r_0}{1-r_0-r_2\left[1-R(\lambda)\right]} \quad (2)$$

$$\text{for a} = 1: \quad R(\lambda)^* = \frac{R(\lambda)}{1 - r_0 - r_2 + r_2\left[r_0 + R(\lambda)\right]} \quad (3)$$

3.3 Incidence 45°, observation 0° (45°: 0°)

$$R(\lambda) = \frac{(1-r_0)(1-\overline{r}_0)\frac{1}{n^2}R(\lambda)^*}{1-r_2R(\lambda)^*} \quad (4)$$

$$R(\lambda)^{*} = \frac{n^{2}\,R(\lambda)}{1 - r_{0} - \bar{r}_{0} + r_{0}\bar{r}_{0} + n^{2}\,r_{2}R(\lambda)} \tag{5}$$

4 Solution of the Kubelka-Munk equations

The Kubelka-Munk theory describes the reflection of a pigmented layer by two constants: absorption [$K(\lambda)$] and scattering [$S(\lambda)$]. It is based on the following assumptions:

a) ideally diffuse radiation distribution on the irradiation side;

b) ideally diffuse radiation distribution in the interior of the layer;

c) no consideration of surface phenomena resulting from the discontinuity in refractive index.

For an infinitely thick, respectively hiding layer with a reflectance of $R(\lambda)_\infty$, the following solutions are found, which allow the determination of the relation between the scattering and the absorption coefficient:

$$\frac{K(\lambda)}{S(\lambda)} = \frac{\left(1 - R(\lambda)_{\infty}\right)^{2}}{2\,R(\lambda)_{\infty}} \equiv F\left(R(\lambda)_{\infty}\right) \tag{6}$$

respectively the inverse:

$$R(\lambda)_{\infty} = 1 + \frac{K(\lambda)}{S(\lambda)} - \sqrt{2\left(\frac{K(\lambda)}{S(\lambda)}\right) + \left(\frac{K(\lambda)}{S(\lambda)}\right)^{2}} \tag{7}$$

For the determination of the scattering and absorption coefficient two different methods can be applied (the Saunderson correction shall be used):

Method 1 Measurement of the reflectance of an infinite thick (respectively hiding) layer and the reflectance $R(\lambda)^{*}$ of a coating of the thickness, h, on a substrate of the reflection $R(\lambda)_{0}^{*}$.

$$a(\lambda) = \frac{1}{2}\left(\frac{1}{R(\lambda)_{\infty}^{*}} + R(\lambda)_{\infty}^{*}\right) \tag{8}$$

$$b(\lambda) = a(\lambda) - R(\lambda)_{\infty}^{*} = \frac{1}{2}\left(\frac{1}{R(\lambda)_{\infty}^{*}} - R(\lambda)_{\infty}^{*}\right) \tag{9}$$

$$S(\lambda) = \frac{1}{b(\lambda)\,h}\,\mathrm{Arcoth}\,\frac{1 - a(\lambda)\,[R(\lambda)^{*} - R(\lambda)_{0}^{*}] + R(\lambda)^{*}\,R(\lambda)_{0}^{*}}{b(\lambda)\,[R(\lambda)^{*} - R(\lambda)_{0}^{*}]} \tag{10}$$

$$K(\lambda) = S(\lambda)\left[a(\lambda) - 1\right] \tag{11}$$

Method 2 This method applies two layers of equal thickness (h) on black and white substances. After the determination of the auxiliary variables $a(\lambda)$, $b(\lambda)$ according to Formulae (12) and (13), either Formula (14) or (15) may be used to calculate the scattering coefficient $S(\lambda)$. The possibility with the least experimental uncertainty should be chosen.

$$a(\lambda) = \frac{[1 + R(\lambda)_{\mathrm{w}}^{*}\,R(\lambda)_{\mathrm{ow}}^{*}][R(\lambda)_{\mathrm{b}}^{*} - R(\lambda)_{\mathrm{ob}}^{*}] + [1 + R(\lambda)_{\mathrm{b}}^{*}R(\lambda)_{\mathrm{ob}}^{*}][R(\lambda)_{\mathrm{ow}}^{*} - R(\lambda)_{\mathrm{w}}^{*}]}{2[R(\lambda)_{\mathrm{b}}^{*}R(\lambda)_{\mathrm{ow}}^{*} - R(\lambda)_{\mathrm{w}}^{*}R(\lambda)_{\mathrm{ob}}^{*}]} \tag{12}$$

$$b(\lambda) = \sqrt{a(\lambda)^2 - 1} \qquad (13)$$

$$\mathrm{S}(\lambda) = \frac{1}{\mathrm{b}(\lambda)\,\mathrm{h}}\ \mathrm{Arcoth}\,\frac{1 - \mathrm{a}(\lambda)[\mathrm{R}(\lambda)_\mathrm{b}^* - \mathrm{R}(\lambda)_\mathrm{ob}^*] + \mathrm{R}(\lambda)_\mathrm{b}^*\ \mathrm{R}(\lambda)_\mathrm{ob}^*}{\mathrm{b}(\lambda)\,[\mathrm{R}(\lambda)_\mathrm{b}^* - \mathrm{R}(\lambda)_\mathrm{ob}^*]} \qquad (14)$$

$$\mathrm{S}(\lambda) = \frac{1}{\mathrm{b}(\lambda)\,\mathrm{h}}\ \mathrm{Arcoth}\,\frac{1 - \mathrm{a}(\lambda)[\mathrm{R}(\lambda)_\mathrm{w}^* - \mathrm{R}(\lambda)_\mathrm{ow}^*] + \mathrm{R}(\lambda)_\mathrm{w}^*\ \mathrm{R}(\lambda)_\mathrm{ow}^*}{\mathrm{b}(\lambda)\,[\mathrm{R}(\lambda)_\mathrm{w}^* - \mathrm{R}(\lambda)_\mathrm{ow}^*]} \qquad (15)$$

$$\mathrm{R}(\lambda)^* = \frac{1 - \mathrm{R}(\lambda)_\mathrm{o}^*\ [\mathrm{a}(\lambda) - \mathrm{b}(\lambda)\ \coth\{\mathrm{b}(\lambda)\ \mathrm{S}(\lambda)\,\mathrm{h}\}]}{\mathrm{a}(\lambda) - \mathrm{R}(\lambda)_\mathrm{o}^* + \mathrm{b}(\lambda)\ \coth\{\mathrm{b}(\lambda)\ \mathrm{S}(\lambda)\,\mathrm{h}\}} \qquad (16)$$

NOTE The formulation of the Kubelka-Munk theory leads to a system of differential equations. The solution can be stated in different ways either by the use of the trigonometric functions used here or by the use of logarithmic functions. They are mathematically equivalent.

5 Determination of relative tinting strength and residual colour difference of coloured pigments

5.1 General

All the methods specified here presuppose, at least approximately, a linear relationship between the concentration of the colorant and the Kubelka-Munk function.

It is assumed that the scattering by the draw-downs being measured is dominated by the white pigment and the absorption by the coloured pigment. All these conditions shall be met to ascertain correct results of the methods described here. The Kubelka-Munk function for the white paste can be neglected in most cases.

5.2 Principle

The reference and test samples are incorporated into white pastes. The corresponding reflectance spectra are measured on opaque draw-downs of the resulting coloured pastes. The appropriate tinting strength criterion is calculated from the measured values.

If the tinting strength criterion values for the reference and test samples differ, the mass fraction of the sample is increased or decreased until the values become equal. This adjustment may be performed either experimentally or mathematically.

If the tinting strength criterion values for the reference and test samples are the same, or after they have been equalized, the residual colour difference between the white reductions of the reference and test samples is calculated from the corresponding reflectance spectra.

A spectrophotometer with d:8° or 8°:d measuring geometry with or without gloss trap, or instruments with 45°:0° or 0°:45° measuring geometry are recommended.

5.3 Procedure

5.3.1 General

The reflectance of an opaque draw-down of the white reduction of the reference sample and the corresponding reflectance of the test sample are measured in the visible spectral range.

5.3.2 Evaluation of absorption at the absorption maximum

The tinting strength criterion is the maximum Kubelka-Munk value. Prerequisite for this method are equal concentrations of reference and test pigments in the white pastes.

Determine the wavelength in the reflectance spectra of the white reductions at which the reflectance is a minimum. From the minimum Saunderson-corrected reflectance R_r* and R_t*, calculate the Kubelka-Munk values $(K/S)_r$ and $(K/S)_t$ for this wavelength by means of Formula (6). The relative tinting strength C_{rel} is then obtained from:

$$C_{\text{rel}} = \left[\frac{\left(\frac{K}{S} \right)_{\text{t}}}{\left(\frac{K}{S} \right)_{\text{r}}} \right] \cdot 100 \qquad (17)$$

NOTE This method does not involve any explicit equalization of the tinting strength criterion. Because of the assumption of linearity between the Kubelka-Munk function and the concentration, equalization is implicit in the formalism of

$$\frac{\left(\frac{K}{S} \right)_{\text{t}}}{\left(\frac{K}{S} \right)_{\text{r}}} = \frac{m_{\text{r}}}{m_{\text{t}}} \qquad (18)$$

Consequently, Formula (17) can be transformed into the defining Formula (19).

$$C_{\text{rel}} = \frac{m_{\text{r}}}{m_{\text{t}}} \cdot 100 \qquad (19)$$

5.3.3 Evaluation of the weighted *K*/*S* sum

The tinting strength criterion is the weighted *K*/*S* sum. From the spectra of the Saunderson-corrected reflectance $R(\lambda)$* for the test and reference samples, calculate the corresponding Kubelka-Munk values $F(\lambda) = (K/S)(\lambda)$ and in each case generate the following weighted sum:

$$T = \sum\nolimits_{(400\text{-}700\text{nm})} g(\lambda) \cdot \mathrm{F}(\lambda) \qquad (20)$$

The function $g(\lambda)$ is a weighting function, defined as the sum of the colour matching functions $\bar{x}(\lambda)$, $\bar{y}(\lambda)$, and $\bar{z}(\lambda)$ for a 10° standard observer (see Reference [4]). This weighting function is an empirical function, but without any theoretical foundation.

The relative tinting strength is calculated from the weighted sums and the mass fractions of the test and reference samples:

$$C_{\text{rel}} = \left[\frac{\left(T_{\text{t}} \cdot m_{\text{r}} \right)}{\left(T_{\text{r}} \cdot m_{\text{t}} \right)} \right] \cdot 100 \qquad (21)$$

$$= \frac{\left(\frac{m_{\text{r}}}{T_{\text{r}}} \right)}{\left(\frac{m_{\text{t}}}{T_{\text{t}}} \right)} \cdot 100$$

NOTE This method does not involve any explicit equalization of the tinting strength criterion. Because of the assumption of linearity between the Kubelka-Munk function and the concentration, and hence also between the Kubelka-Munk function and the tinting strength criterion *T*, equalization is implicit in the formalism of Formula (21).

If the difference between the tinting strength criterion of the reference sample T_r and that of the test sample T_t is greater than 15 %, the mass fraction of the test sample should be varied accordingly.