OIV-MA-AS2-11 Determination of chromatic characteristics according to CIELab

Type I method

1. Introduction

The colour of a wine is one of the most important visual features available to us, since it provides a considerable amount of highly relevant information.

Colour is a sensation that we perceive visually from the refraction or reflection of light on the surface of objects. Colour is light—as it is strictly related to it—and depending on the type of light (illuminating or luminous stimulus) we see one colour or another. Light is highly variable and so too is colour, to a certain extent.

Wine absorbs a part of the radiations of light that falls and reflects another, which reaches the eyes of the *observer*, making them experience the sensation of colour. For instance, the sensation of very dark red wines is almost entirely due to the fact that incident radiation is absorbed by the wine.

1.1. Scope

The purpose of this spectrophotometric method is to define the process of measuring and calculating the *chromatic characteristics* of wines and other beverages derived from *trichromatic components*: X, Y and Z, according to the *Commission Internationale de l'Eclairage* (CIE, 1976), by attempting to imitate real observers with regard to their sensations of colour.

1.2. Principle and definitions

The colour of a wine can be described using 3 attributes or specific qualities of visual sensation: tonality, luminosity and chromatism.

Tonality—colour itself—is the most characteristic: red, yellow, green or blue. *Luminosity* is the attribute of visual sensation according to which a wine appears to be more or less luminous. However, *chromatism,* or the *level of colouring,* is related to a higher or lower intensity of colour. The combination of these three concepts enables us to define the multiple shades of colour that wines present.

The *chromatic characteristics* of a wine are defined by the *colorimetric* or *chromaticity coordinates* (Fig. 1): *clarity* (L^*), *red/green colour component* (a^*), and *blue/yellow colour component* (b^*); and by its *derived magnitudes*: *chroma* (C^*), *tone* (H^*) and *chromacity* [(a^*, b^*) or (C^*, H^*)]. In other words, this CIELab colour or space

system is based on a sequential or continuous Cartesian representation of 3 orthogonal axes: L^*, a^* and b^* (Fig. 2 and 3). Coordinate L^* represents clarity (L^* = 0 black and L^* = 100 colourless), a^* green/red colour component (a^*>0 red, a^*<0 green) and b^* blue/yellow colour component (b^*>0 yellow, b^*<0 blue).

1.2.1. Clarity

Its symbol is L^* and it is defined according to the following mathematical function:

$$L* = 116(Y/Y_n)^{1/3} - 16 \quad (1)$$

Directly related to the visual sensation of luminosity.

1.2.2. Red/green colour component

Its symbol is a^* and it is defined according to the following mathematical function:

$$a* = 500[(X/X_) - (Y/Y_n)] \quad (I)$$

1.2.3. Yellow/blue colour component

Its symbol is b^* and it is defined according to the following mathematical function:

$$b* = 200 - \left[(Y/Y_n)^{\frac{1}{3}} - (Z/Z_n)^{1/3}\right] \quad (I)$$

1.2.4. Chroma

The chroma symbol is C^* and it is defined according to the following mathematical function:

$$C* = \sqrt{(a*^2 + b*^2)}$$

1.2.5. Tone

The tone symbol is H^*, its unit is the sexagesimal degree (°), and it is defined according to the following mathematical function:

$$H* = tg^{-1}(b^*/a^*)$$

1.2.6. Difference of tone between two wines

The symbol is ΔH* and it is defined according to the following mathematical function:

$$\Delta H* = \sqrt{(\Delta E*)^2 - (\Delta L*)^2 - (\Delta C*)^2}$$

(I) See explanation Annex I

1.2.7. Overall colorimetric difference between two wines

The symbol is ΔE* and it is defined according to the following mathematical functions:

$$\Delta E* = \sqrt{(\Delta L*)^2 + (\Delta a*)^2 + (\Delta b*)^2} = \sqrt{(\Delta L*)^2 + (\Delta C*)^2 + (\Delta H*)^2}$$

1.3. Reagents and products

Distilled water.

1.4. Apparatus and equipment

Customary laboratory apparatus and, in particular, the following:

1.4.1. Spectrophotometer to carry out transmittance measurements at a wavelength of between 300 and 800 nm, with illuminant D65 and observer placed at 10°. Use apparatus with a resolution equal to or higher than 5 nm and, where possible, with scan.

1.4.2. Computer equipment and suitable programme which, when connected to the spectrophotometer, will facilitate calculating colorimetric coordinates (L^*, a^* and b^*) and their derived magnitudes (C^* and H^*).

1.4.3. Glass cuvettes, available in pairs, optical thickness 1, 2 and 10 mm.

1.4.4. Micropipettes for volumes between 0.020 and 2 ml.

1.5. Sampling and sample preparation

Sample taking must particularly respect all concepts of homogeneity and representativity.

If the wine is dull, it must be clarified by centrifugation. For young or sparkling wines, as much carbon dioxide as possible must be eliminated by vacuum stirring or using a sonicator.

1.6. Procedure

- Select the pair of cuvettes for the spectrophotometric reading, ensuring that the upper measurement limit within the linear range of the spectrophotometer is not exceeded. By way of indication, for white and rosé wines it is recommended to use cuvettes with 10 mm of optical thickness, and for red wines, cuvettes with 1 mm optical thickness.

After obtaining and preparing the sample, measure its transmittance from 380 to 780 nm every 5 nm, using distilled water as a reference in a cuvette with the same optical thickness, in order to establish the base line or the white line. Choose illuminant D65 and observer 10°

If the optical thickness of the reading cuvette is under 10 mm, the transmittance must be transformed to 10 mm before calculating: L^*, a^*, b^*, C^* and H^*.

Summary:

Spectral measurements in transmittance from 780 to 380 nm
Interval: 5 nm
Cuvettes: use appropriately according to wine intensity: 1 cm (white and rosé wines) and 0.1 cm (red wines)
Illuminant D65
Observer reference pattern 10º

1.7. Calculations

The spectrophotometer must be connected to a computer programme to facilitate the calculation of the colorimetric coordinates (L^*, a^* and b^*) and their derived magnitudes (C^* and H^*), using the appropriate mathematical algorithms.

In the event of a computer programme not being available, see Annex I on how to proceed.

1.8. Expression of results

The colorimetric coordinates of wine will be expressed according to the recommendations in the following table.

Colorimetric coordinates	Symbol	Unit	Interval	Decimals
Clarity	L^*		0-100 0 black 100 colourless	1
Red/green colour component	a^*		>0 red <0 green	2
Yellow/blue colour component	b^*		>0 yellow <0 blue	2
Chroma	C^*			2
Tone	H^*	º	0-360º	2

1.9. Numerical Example

Figure 4 shows the values of the colorimetric coordinates and the chromaticity diagram of a young red wine for the following values:

X = 12.31; Y = 60.03 and Z = 10.24

L* = 29.2

a* = 55.08

b* = 36.10

C* = 66.00

H* = 33.26°

2. Accuracy

The above data were obtained from two interlaboratory tests of 8 samples of wine with blind duplicates of progressive chromatic characteristics, in accordance with the recommendations of the harmonized protocol for collaborative studies, with a view to validating the method of analysis.

Colorimetric coordinate L* (clarity, 0-100)

Sample Identification	A	B	C	D	E	F	G	H
Year of interlaboratory test	2004	2002	2004	2004	2004	2004	2002	2004
No. of participating laboratories	18	21	18	18	17	18	23	18
No. of laboratories accepted after aberrant value elimination	14	16	16	16	14	17	21	16
Mean value ($\bar{x}$)	96.8	98.0	91.6	86.0	77.4	67.0	34.6	17.6
Repeatability standard deviation (s_r)	0.2	0.1	0.2	0.8	0.2	0.9	0.1	0.2
Relative repeatability standard deviation (RSD_r) (%)	0.2	0.1	0.3	1.0	0.3	1.3	0.2	1.2

Repeatability limit (r) (2.8 x s_r)	0.5	0.2	0.7	2.2	0.7	2.5	0.2	0.6
Reproducibility standard deviation (s_R)	0.6	0.1	1.2	2.0	0.8	4.1	1.0	1.0
Relative reproducibility standard deviation (RSD_R) (%)	0.6	0.1	1.3	2.3	1.0	6.1	2.9	5.6
Reproducibility limit (R) (2.8 x s_R)	1.7	0.4	3.3	5.5	2.2	11.5	2.8	2.8

Colorimetric coordinate a* (green/red)

Sample Identification	A	B	C	D	E	F	G	H
Year of interlaboratory	2004	2002	2004	2004	2004	2004	2002	2004
No. of participating laboratories	18	21	18	18	17	18	23	18
No. of laboratories accepted after aberrant value elimination	15	15	14	15	13	16	23	17
Mean value ($\bar{X}$)	-0.26	-0.86	2.99	11.11	20.51	29.29	52.13	47.55
Repeatability standard deviation (s_r)	0.17	0.01	0.04	0.22	0.25	0.26	0.10	0.53
Relative repeatability standard deviation (RSD_r) (%)	66.3	1.4	1.3	2.0	1.2	0.9	0.2	1.1
Repeatability limit (r) (2.8 x s_r)	0.49	0.03	0.11	0.61	0.71	0.72	0.29	1.49
Reproducibility standard deviation (s_R)	0.30	0.06	0.28	0.52	0.45	0.98	0.88	1.20

Relative reproducibility standard deviation (RSD_R) (%)	116.0	7.5	9.4	4.7	2.2	3.4	1.7	2.5
Reproducibility limit (R) (2.8 x s_R)	0.85	0.18	0.79	1.45	1.27	2.75	2.47	3.37

Colorimetric coordinate b* (blue/yellow)

Sample Identification	A	B	C	D	E	F	G	H
Year of interlaboratory	2004	2002	2004	2004	2004	2004	2002	2004
No. of participating laboratories	17	21	17	17	17	18	23	18
No. of laboratories accepted after aberrant value elimination	15	16	13	14	16	18	23	15
Mean value ($\bar{x}$)	10.95	9.04	17.75	17.10	19.68	26.51	45.82	30.07
Repeatability standard deviation (s_r)	0.25	0.03	0.08	1.08	0.76	0.65	0.15	0.36
Relative repeatability standard deviation (RSD_r) (%)	2.3	0.4	0.4	6.3	3.8	2.5	0.3	1.2
Repeatability limit (r) (2.8 x s_r)	0.71	0.09	0.21	3.02	2.12	1.83	0.42	1.01
Reproducibility standard deviation (s_R)	0.79	0.19	0.53	1.18	3.34	2.40	1.44	1.56
Relative reproducibility standard deviation (RSD_R) (%)	7.2	2.1	3.0	6.9	16.9	9.1	3.1	5.2
Reproducibility limit (R) (2.8 x s_R)	2.22	0.53	1.47	3.31	9.34	6.72	4.03	4.38

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Appendix 1

In formal terms, the trichromatic components X, Y, Z of a colour stimulus result from the integration, throughout the visible range of the spectrum, of the functions

obtained by multiplying the relative spectral curve of the colour stimulus by the colorimetric functions of the reference observer. These functions are always obtained by experiment. It is not possible, therefore to calculate the trichromatic components directly by integration. Consequently, the approximate values are determined by replacing these integrals by summations on finished wavelength intervals.

$$X = K \sum_{(\lambda)} T_{(\lambda)} S_{(\lambda)} \overline{X}_{10(\lambda)} \Delta_{(\lambda)}$$

$$Y = K \sum_{(\lambda)} T_{(\lambda)} S_{(\lambda)} \overline{Y}_{10(\lambda)} \Delta_{(\lambda)}$$

$$Z = K \sum_{(\lambda)} T_{(\lambda)} S_{(\lambda)} \overline{Z}_{10(\lambda)} \Delta_{(\lambda)}$$

$$K = 100 / \sum_{(\lambda)} S_{(\lambda)} \overline{Y}_{10(\lambda)} \Delta_{(\lambda)}$$

T (□) is the measurement of the transmittance of the wine measured at the wavelength □ expressed at 1 cm from the optical thickness.

$\Delta_{(\lambda)}$ is the interval between the value of □ at which T (□) is measured

S (□): coefficients that are a function of □ and of the illuminant (Table 1).

$\overline{X}_{10(\lambda)}; \overline{Y}_{10(\lambda)}; \overline{Z}_{10(\lambda)}$: coefficients that are a function of □ and of the observer. (Table 1)

The values of Xn, Yn, and Zn represent the values of the perfect diffuser under an illuminant and a given reference observer. In this case, the illuminant is D65 and the observer is higher than 4 degrees.

X_n = 94.825; Y_n = 100; Z_n = 107.381

This roughly uniform space is derived from the space CIEYxy, in which the trichromatic components X, Y, Z are defined.

The coordinates L*, a* and b* are calculated based on the values of the trichromatic components X, Y, Z, using the following formulae.

$L^* = 116 (Y / Y_n)^{1/3}$ □ 16 where $Y/Yn > 0.008856$

$L^* = 903.3 (Y / Y_n)$ where $Y / Y_n <$ ó = 0.008856

a* = 500 [f(X / X_n) □ f(Y / Y_n) □

b* = 200 [f(Y / Y_n) □ f(Z / Z_n) □

f(X / X_n) = (X / X_n)$^{1/3}$ where (X / X_n) > 0.008856

f(X / X_n) = 7.787 (X / X_n) + 16 / 166 where (X / X_n) < ó = 0.008856

f(Y / Y_n) = (Y / Y_n)$^{1/3}$ where (Y / Y_n) > 0.008856

f(Y / Y_n) = 7.787 (Y / Y_n) + 16 / 116 where (Y / Y_n) < ó = 0.008856

f(Z / Z_n) = (Z / Z_n)$^{1/3}$ where (Z / Z_n) > 0.008856

f(Z / Z_n) = 7.787 (Z / Z_n) + 16 / 116 where (Z / Z_n) < ó = 0.008856

The total colorimetric difference between two colours is given by the CIELAB colour difference

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

In the CIELAB space it is possible to express not only overall variations in colour, but also in relation to one or more of the parameters L*, a* and b*. This can be used to define new parameters and to relate them to the attributes of the visual sensation.

Clarity, related to luminosity, is directly represented by the value of L*.

Chroma: $C* = (a*^2 + b*^2)^{1/2}$ defines the chromaticness.

The angle of hue: H* = tg^{-1}(b*/a*) (expressed in degrees); related to hue.

The difference in hue: $\Delta H* = [(\Delta E*)^2 + (\Delta L*)^2 + (\Delta C*)^2])^{1/2}$

For two unspecified colours, Δ C* represents their difference in chroma; Δ L*, their difference in clarity, and Δ E*, their overall variation in colour. We thus have:

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

Table 1.

Wavelength (□) nm.	$S_{(\lambda)}$	$\bar{X}_{10(\lambda)}$	$\bar{Y}_{10(\lambda)}$	$\bar{Z}_{10(\lambda)}$
380	50.0	0.0002	0.0000	0.0007

385	52.3	0.0007	0.0001	0.0029
390	54.6	0.0024	0.0003	0.0105
395	68.7	0.0072	0.0008	0.0323
400	82.8	0.0191	0.0020	0.0860
405	87.1	0.0434	0.0045	0.1971
410	91.5	0.0847	0.0088	0.3894
415	92.5	0.1406	0.0145	0.6568
420	93.4	0.2045	0.0214	0.9725
425	90.1	0.2647	0.0295	1.2825
430	86.7	0.3147	0.0387	1.5535
435	95.8	0.3577	0.0496	1.7985
440	104.9	0.3837	0.0621	1.9673
445	110.9	0.3867	0.0747	2.0273
450	117.0	0.3707	0.0895	1.9948
455	117.4	0.3430	0.1063	1.9007
460	117.8	0.3023	0.1282	1.7454
465	116.3	0.2541	0.1528	1.5549
470	114.9	0.1956	0.1852	1.3176
475	115.4	0.1323	0.2199	1.0302
480	115.9	0.0805	0.2536	0.7721
485	112.4	0.0411	0.2977	0.5701

490	108.8	0.0162	0.3391	0.4153
495	109.1	0.0051	0.3954	0.3024
500	109.4	0.0038	0.4608	0.2185
505	108.6	0.0154	0.5314	0.1592
510	107.8	0.0375	0.6067	0.1120
515	106.3	0.0714	0.6857	0.0822
520	104.8	0.1177	0.7618	0.0607
525	106.2	0.1730	0.8233	0.0431
530	107.7	0.2365	0.8752	0.0305
535	106.0	0.3042	0.9238	0.0206
540	104.4	0.3768	0.9620	0.0137
545	104.2	0.4516	0.9822	0.0079
550	104.0	0.5298	0.9918	0.0040
555	102.0	0.6161	0.9991	0.0011
560	100.0	0.7052	0.9973	0.0000
565	98.2	0.7938	0.9824	0.0000
570	96.3	0.8787	0.9556	0.0000
575	96.1	0.9512	0.9152	0.0000
580	95.8	1.0142	0.8689	0.0000
585	92.2	1.0743	0.8256	0.0000
590	88.7	1.1185	0.7774	0.0000

595	89.3	1.1343	0.7204	0.0000
600	90.0	1.1240	0.6583	0.0000
605	89.8	1.0891	0.5939	0.0000
610	89.6	1.0305	0.5280	0.0000
615	88.6	0.9507	0.4618	0.0000
620	87.7	0.8563	0.3981	0.0000
625	85.5	0.7549	0.3396	0.0000
630	83.3	0.6475	0.2835	0.0000
635	83.5	0.5351	0.2283	0.0000
640	83.7	0.4316	0.1798	0.0000
645	81.9	0.3437	0.1402	0.0000
650	80.0	0.2683	0.1076	0.0000
655	80.1	0.2043	0.0812	0.0000
660	80.2	0.1526	0.0603	0.0000
665	81.2	0.1122	0.0441	0.0000
670	82.3	0.0813	0.0318	0.0000
675	80.3	0.0579	0.0226	0.0000
680	78.3	0.0409	0.0159	0.0000
685	74.0	0.0286	0.0111	0.0000
690	69.7	0.0199	0.0077	0.0000
695	70.7	0.0138	0.0054	0.0000

700	71.6	0.0096	0.0037	0.0000
705	73.0	0.0066	0.0026	0.0000
710	74.3	0.0046	0.0018	0.0000
715	68.0	0.0031	0.0012	0.0000
720	61.6	0.0022	0.0008	0.0000
725	65.7	0.0015	0.0006	0.0000
730	69.9	0.0010	0.0004	0.0000
735	72.5	0.0007	0.0003	0.0000
740	75.1	0.0005	0.0002	0.0000
745	69.3	0.0004	0.0001	0.0000
750	63.6	0.0003	0.0001	0.0000
755	55.0	0.0002	0.0001	0.0000
760	46.4	0.0001	0.0000	0.0000
765	56.6	0.0001	0.0000	0.0000
770	66.8	0.0001	0.0000	0.0000
775	65.1	0.0000	0.0000	0.0000
780	63.4	0.0000	0.0000	0.0000

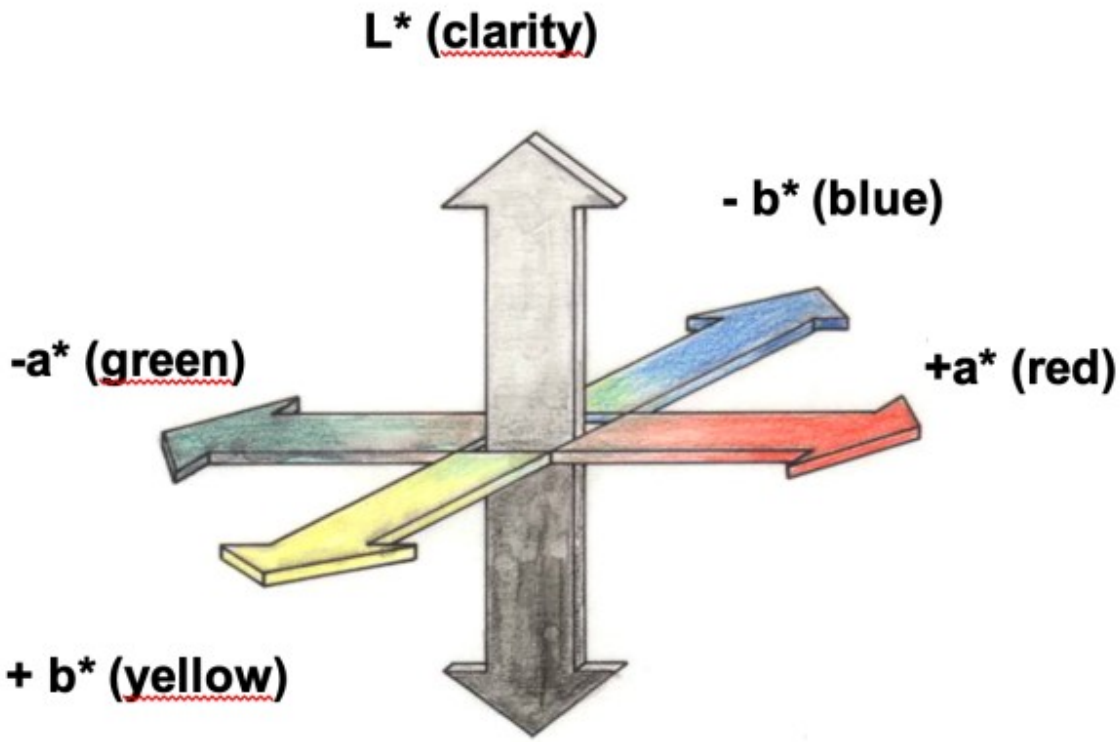


Figure 1. Diagram of colourimetric coordinates according to Commission Internationale de l'Eclairage (CIE, 1976)

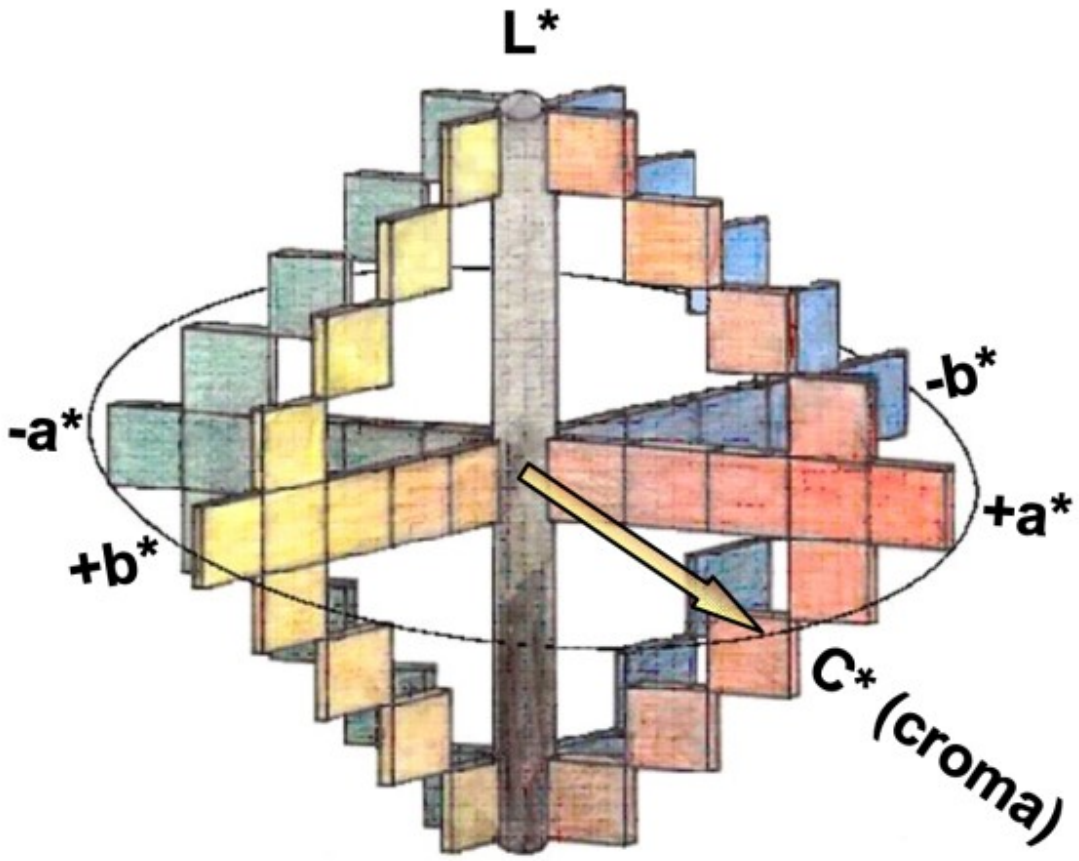


Figure 2. CIELab colourspace, based on a sequential or 3 orthogonal axis continual Cartesian representation L*, a* y b*

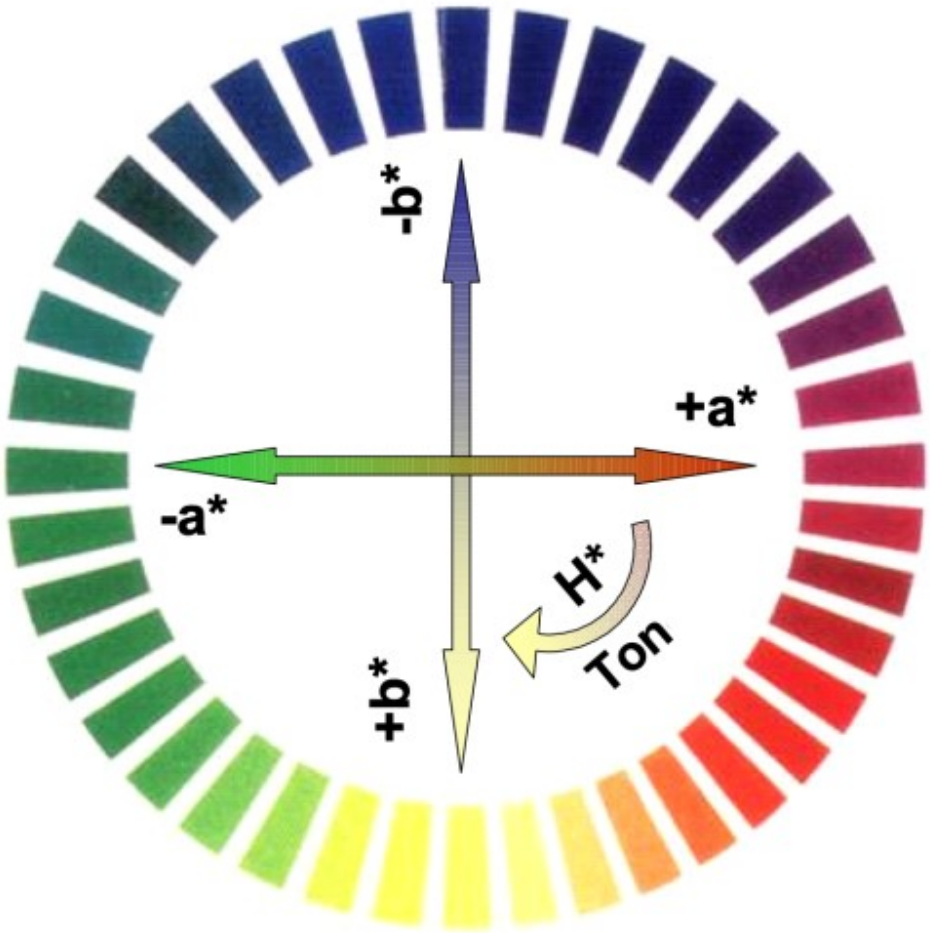


Figure 3. Sequential diagram and/or continuation of a and b colourimetric coordinates and derived magnitude, such as tone (H*)

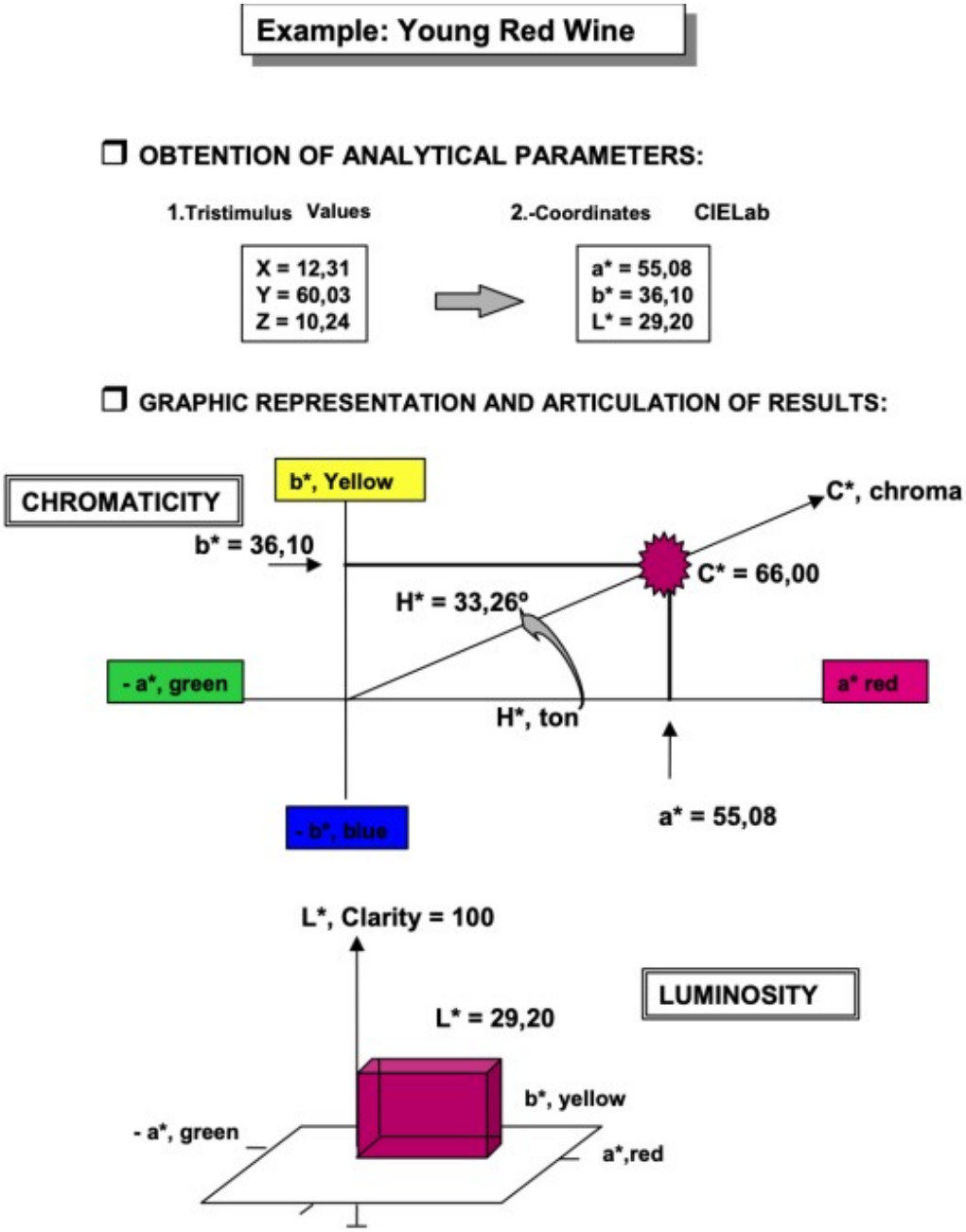


Figure 4. Representation of colour of young red wine used as an example in Chapter 1.8 shown in the CIELab three dimensional diagram.