Chromatic parameters evaluation during red wines pigmentation

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Abstract

The colour represents an important parameter of wine quality. This characterises sort, type, composition and age of wine. Unlike white wines, the red wine colour is determined by the presence of some specific substances –anthocyanic pigments. A big importance on the colour of red wine presents tenant substances, acidity, metals, reductive substances. The colour of wine is affected by several factors, among the more important being grape variety, pH, temperature, oenological treatments and aging. Research has been made on various sorts of wines from the Tighina, Republic of Moldova and Bujor Hills, Romania respectively. Tristimulus colorimetry (CIEXYZ, CIELAB colour spaces) proved to be a useful tool for the chromatic characterization of studied wines.

Keywords: Tristimulus colorimetry, CIEXYZ and CIELAB colour space, color intensity, hue

Rezumat

Culoarea reprezintă un indice important al calităţii vinurilor. Aceasta caracterizează soiul, tipul, compoziţia şi vârsta vinului. Spre deosebire de vinurile albe, culoarea vinurilor roşii este determinată de prezenţa unor substanţe specifice - pigmenţii antocianici. Substanţele tanante, aciditatea, metalele, substanţele reducătoare prezintă o importanţă deosebită asupra culorii vinurilor roşii. Culoarea vinurilor este influenţată de câţiva factori, dintre care cei mai importanţi sunt tipul de struguri, pH-ul, temperatura, tratamentele oenologice şi durata maturării. Cercetările au fost efectuate pe soiuri diferite de vin din Tighina, Republica Moldova şi din podgoria Dealul Bujorului, România. Utilizarea metodei „Tristimulus colorimetry” s-a dovedit a fi un instrument util în vederea caracterizării cromatice ale vinurilor studiate.

Cuvinte cheie: Tristimulus colorimetry, spaţii coloristice CIEXYZ şi CIELAB, intensitatea colorantă, tenta

1. Introduction

Wine-growing in Romania has some characteristics which make it more special than wine-growing in other countries. These characteristics are marked on the selection of grape products and wines that can be obtained. Wine-growing in Romania is a micro food of wine-growing; it can offer different conditions, so that the wine selection possibility is very wide. Our research in this study has been conducted on different sorts of red wine, destined for family consumption: two wines from the Republic of Moldova, Chisinau vineyard and one wine from Romania, choose from the Bujor Hills vineyard, Bujor wine-growing centre, Galati.

The maturation phase begins after fermentation is complete and the wine is pressed, this takes up until the wine is bottled. Most red wines are matured for several months or years in oak barrels, after being bottled they are first arranged and stabilized. In all this time, mostly sensorial changes are the coloured ones and the texture of the wine, which are due to the polymerisation of the phenols.

In grapes, mineral and organic acids can be found, which can vary in quantity and the proportion between them, organic acids are in big quantities, in free state or under acid or neutral salts; e.g. there have been identified over 50 organic acids of which the most important tartric acid, malic, citric, oxalic, fumaric, ascorbic etc (Nicolai *et al*., 2000).

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The better knowledge of the pH represents a special importance in the red wine technology, because it directly influences the taste properties, the clarity and colour and it determines the conditions of development of useful and pathogenic micro organisms, as well as the development of physical-chemical, chemical and biological processes which take place in wine on it's evolution.

For wines, the pH value is a quality parameter because it is not known exactly which of the components with acid character from the food complex has dissociated stronger, knowing that stronger acids relegate the ionization of weaker acids (normal effect in reactions at chemical balance). On top of this the pH becomes essential in technology and in wine characteristics (Pellerin *et al*., 1995). The value of *p*H corresponds to the actual concentration level of $[H^+]$ from momentary ionization of present acids. That is why *p*H represents the real or actual acidity.

Colour is one of the main organoleptic characteristics used to establish the quality and acceptability of wines. The use of sensory panels to measure colour is complex, time-consuming, expensive and subject to error owing to variability in human judgment. It would thus be useful to have an objective system for the measurement of the spectral characteristics and colour coordinates of samples.

The objective apreciation of colour is using photocolorimetric methods or spectrophoto-colorimetric, expresing being made through absorbtion of some radiations of the visibil spectrum. In the same maner the most precise method of colour exprimation in wine is the method that gives back the absorbtion for all colours which form the characteristic colour of the food product. Because this method is more laborious in practice there can be used simpler methods which express maximum absorbtion of some radiations of a characteristic wavelength.

From wine VIS spectra it is possible to calculate the CIE tristimulus values (X,Y,Z). Several mathematical transformations of these values allow the three coordinates to be transformed to describe the colour. Such coordinates relate to lightness (L in the CIE L a*b* system or Y in xyY system) and the two others relate to chromaticity (a*, b* in the CIE La*b* system and xy in the xyY system). The red colour of wines is due mainly to both anthocyanins and polymeric pigments and depends on several factors, including the age of the wine; but the measurement of the age of a wine is an unresolved problem (Archier *et al*., 1993; Fulcrand *et al*., 1996).

The CIEXYZ system were used by Bakker *et al.* (1993) to evaluate the change of red wines colour during aging. Thus, there is no uniformity regarding a method or illuminant to measure colour in wines. The aim of the present work was to establish the colour changes of some red wines and to compare the two most widely used systems (CIE L*a*b* and CIEXYZ) to determine which is most suitable for research into the colour of studied red wines. For that purpose, CIE La*b*, xyY and XYZ systems were assessed. Furthermore, correlations between these objective measures and sensory judgements of colour were estimated.

2. Materials and methods

2.1. Materials

Samples. All wine categories have been provided by wine producers, respectively by grape orchards owners outside the two demarked zones Tighina vineyard (the samples I_A and I_B) and Bujor Hills vineyard (the sample II). Wines have been kept in iodometric bottles 250 mL on the constant temperature of 4°C.

Reagents. The potassium metabisulphit 20%, for polymer pigment colour determination, as well as the buffer solutions reactive were from the analytic reactive class or either pure. Buffer solutions: saturate solution of acid tartric potassium (*p*H = 3.57 at 20°C, 3.56 at 25°C and 3.55 at 30°C), 0.05M solution of ftalic acid potassium (*p*H = 4.003 at 20°C, 4.008 at 25°C and 4.015 at 30°C) and solution containing KH_2PO_4 and K_2HPO_4, according to standardized analysis methods (*p*H = 6.88 at 20°C, 6.86 at 25°C and 6.85 at 30°C).

Apparatus. An S 750i UV-Visible spectrophoto-meter (A.C.I. Orssey-Paris, France), equipped with a computer for calculation of the chromatic parameters, was used to perform the absorbance and transmittance measurements. A MP 220 Digital *p*H Meter equipped with a combined glass-calomel electrode and 0,001 m cells were also used for the experimentation.

2.2. Methods

To determine the main physical-chemical characteristics there have been used standardized analysis methods, in concordance with C.E. 1493/99 reglementation of the European Union Council from May 14th 1999 (Somers *et al*., 1988).

Wine maturation has been studied through average methods: total acidity determination, expressed in H_2SO_4 (g/L) and tartric acid (g/L), polymer pigment colour determination, intensity color and tint and organoleptic appreciation (Recueil International des Methodes d'analyses des Vins et des Mouts, 2006).

The spectral transmittances in the visible spectra (λ=380-780 nm) were measured with the spectrophotometer. To obtain the tristimulus values, recommendations made by the Commission Internationale de l'Eclairage: CIE 1931, 1964 (x, y) system (CIEXYZ), CIE 1976 (L*a*b*) space (CIELAB), CIE 1986 and CIE 1995 were applied, using as references the CIE (CIE 1995). Standard Illuminant C and distilled water as reference blank.

The data were analyzed by the Statistica Software, and the correlations between color parameters were obtained.

The sensory evaluation was carried out by a panel of ten trained judges. The panelists marked the samples for lightness and redness, giving a score between 1 and 9 in each case. This was on a scale from 1 (extremely dark) to 9 (extremely light) on the lightness scale and from 1 (no redness) to 9 (very red) on the other scale. As no significant differences were found between panelists, averages were taken for each sample.

3. Results and discussion

Under organoleptic aspect the studied wines have red or redish color with a pleasant specific taste of the sort flavour, pleasant taste and freshness. The organoleptic appreciations were from tannic and astringent to agreeable and hard.

The total acidity has extreme limits between 3 and 4.5 in sulfuric acid. On the other hand, if may be the case of wines from Tighina their pH (and total acidity) vary in time of maturation period somehow shuffled (min/max: 3.53 and 3.68, and 3.11 and 3.37), this does not happen in the case of wine from Bujor Hills vineyard when *p*H is from 3.11 to 3.36.

It has to be specified the fact that nevertheless total acidity variation but pH variation take place in very small domain. Short in color seems to be the sort belonging to Bujor Hills vineyard. The organoleptic apreciation on wine underlined the most precious quality for wine I_B which turned out to be more pleasant at taste.

The barrel taste, noticed at wine I_A, is a dry taste, a wooden taste. It distinguishes a pleasing wooden taste, given by new wood and that associates later on with fine red wines blucher. Its astringency is given by the presence of the tenant substances in big quantities causing the sensation of contracting the mucous membrane in the stomach. In case the wine has a high content of tannins, the wine is tough, firm, rough. These defects appear when the maceration – fermentation takes place with the chusters or in the case of press wines.

For simple and global characterization of red wine colour, on the bases of optic densities at bandwidth characteristics, we foresaw a series of indexes, out of which we recall: coloured intensity, tint and the weight of every colour. Red wine colour determination can be evaluated by adding the 3 components: red, yellow and blue. The red component (absorbance to 520 nm or DO_{520}) is ascribed to free anthocyans under the form of flavilium cations and combinations of anthocyans-tannins in older wines. The yellow component (DO_{420}) is ascribed to tannins and anthocyans degradation products. The blue component (DO_{620}) is ascribed to free anthocyans under the chinonic form or combinations between tannins and anthocyans.

From figure 1 it could be noticed that regarding the quantity of polymer pigments existing in wine, this recorded subtraction values from the old wine to the tender one.

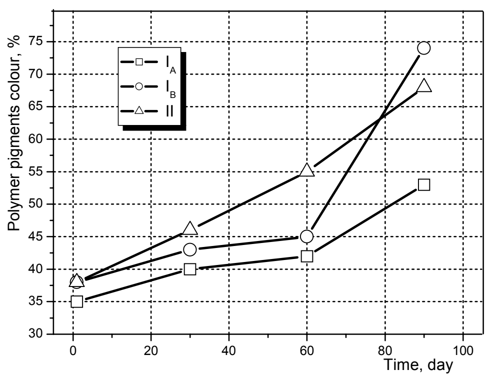

Figure 1. Variation of polymer pigments colour in time

Also, it has to say that in time of maturation period, another two main phys-chemical indexes on wine change, respectively the color intensity and hue.

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Figures 2 and 3 reveal the fact that the color intensity drops for red wine, whilst the tint for red wine intensifyes. At brut wine II, for example, the color intensity recorded values of 1.084 in order to reach after three months a value of 0.383.

The color intensity is short on the sort at Bujor Hills vineyard. The color diminuation is due to the disappereance of momentary anthocyans, in the phase of maturation.

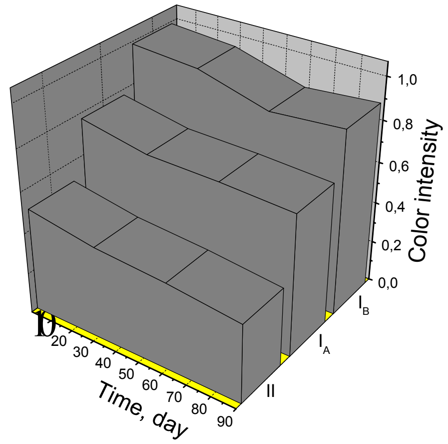

Figure 2. The colour intensity dynamics whilst maturation

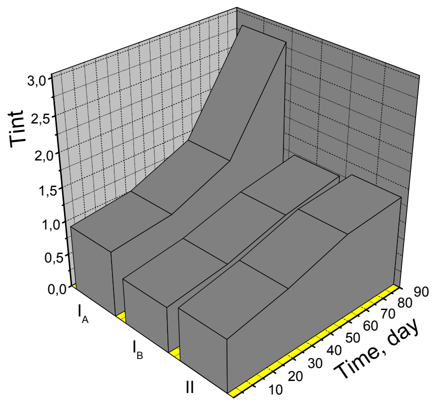

Figure 3. The tint dynamics whilst maturation

The colour intensity is correlated with quantitative variation of anthocyans.

In time of red wine maturation, due to the fact that DO at 420 nm is increasing and DO at 520 nm is decreasing, the tint is emphasizes, so that it grows from 0.969 and 0.677 and 0.783, values which correspond to young red wines, at 2.822 and 1.227 and 1.335 are values which correspond to after 3 month maturation red wines.

Decreasing the extinction at 520 nm it is blamed on precipitation of the more numerous condensed tannins. Colour modification in time of maturation is due as well as to red components diminutions as well as to yellow component intensification occurred after tenant substances in grapes oxidize (figure 4 and table 1).

Table 2 and 3 shows the results obtained for objective colour evaluation carried out in CIE systems and calculated for the illuminants C.

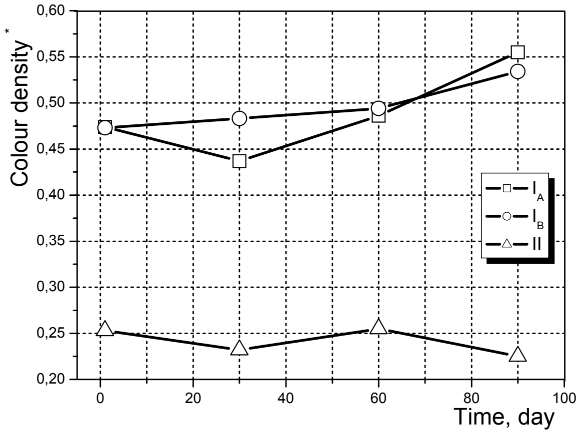

Figure 4. Maturation effect on colour density of red wine;
∗ Colour density = $DO_{420} + DO_{620}$ (Recueil International des Methodes d'analyses des Vins et des Mouts, 2006)

***Table* 1.** The weight colour to global colour of wines

Sample	Time, days	Weight of color		
		% yellow	% red	% purple
I_A	1	0.374	0.386	0.239
	30	0.298	0.276	0.144
	60	0.625	0.430	0.342
	90	0.513	0.181	0.269
I_B	1	0.362	0.534	0.129
	30	0.874	0.574	0.208
	60	0.567	0.529	0.136
	90	0.510	0.416	0.106
II	1	0.463	0.591	0.137
	30	0.304	0.313	0.035
	60	0.232	0.185	0.052
	90	0.551	0.212	0.036

These is an illuminant which is the most frequently used nowadays among those selected by the CIE in order to standardize lightning conditions of colour measurement (Calvo, 1996). The colour parameters determined in the table 2 were as follows tristimulus

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values, X, Y, Z, chromaticity coordinates x,y,z, obtained by standardizing tristimulus values, dominant wavelength, defined as the wavelength of the monochromatic stimulus that, when mixed some specified achromatic stimulus, matches the given stimulus in colour. It was determined following the method proposed by Heredia and Guzman (1992) and excitation purity, which correlates loosely with saturation of the colour perceived under ordinary observing conditions and indicates how far the chromaticity point is displaced towards the spectrum locus. In the table 3 colour coordinates L represents the lightness and a^* and b^* indicate the change in hue from red to green and from yellow to blue, respectively. Also, C^* represent chroma, a correlate for saturation and h_{ab} is the hue angle, a useful quantity in specifying hue numerically.

All parameters showed some variability between wine samples. By analising table 2 and table 3 it could be seen that small but significant differences between chromatic characteristics for all wines sample studied.

This results shows that both systems (CIEXYZ and CIELAB) could be used to evaluate changes in lightness (Y and L, respectively), this parameter being the most useful to show colour changes. In all cases a slight increase of this parameter was determined.

However, the importance of red parameter not be ignored. In our study, a^* (redness) and b^* (yellowness) showed the variation of the wines colour whilst maturation in the XYZ and LAB CIE systems, respectively.

Dominant wavelengths for sample I, for example, are located in the λ_d = 561–592.5 nm interval, with excitation purity values from 5.66% to 21.33%, while for sample II this variation is more large.

Table 2. The experimental results of wine samples obtained according to CIE 1964 (x, y) colour system (CIEXYZ)

Sample	Day	Tristimulus values			Chromaticity coordinates			Dominant wavelength λ_d, nm	Excitation purity p_e, %
		X	Y	Z	x	y	z		
I_A	1	55.671	53.657	60.822	0.327	0.315	0.357	592.5	5.66
	30	59.801	56.689	60.062	0.338	0.321	0.340	586	11.28
	60	59.696	61.878	60.350	0.328	0.340	0.332	565.5	14.42
	90	61.740	70.714	56.238	0.327	0.374	0.298	561	21.33
I_B	1	51.646	40.059	50.300	0.364	0.282	0.354	498.5*	21.21
	30	53.886	42.651	46.994	0.375	0.297	0.327	497*	14.44
	60	57.232	49.912	47.632	0.369	0.322	0.308	601	17.52
	90	55.825	48.781	43.942	0.375	0.328	0.295	593.5	21.49
II	1	33.012	40.560	67.980	0.233	0.286	0.480	487	33.85
	30	73.675	63.164	66.974	0.361	0.309	0.328	520	12.04
	60	74.354	67.537	67.262	0.355	0.323	0.322	592	14.29
	90	77.490	69.645	67.134	0.362	0.325	0.313	594.5	15.67

* Values corresponding to complementary wavelength λ_c (colour points located in the non-spectral purples triangle from chromaticity diagram)

Table 3. CIELAB coordinates of wine samples

Sample	Day	L	a^*	b^*	a^*/b^*	$(a^*/b^*)^2$	C^*	H^*	s^*
I_A	1	78.261	7.801	2.162	3.608	13.019	8.094	15.490	0.103
	30	80.004	10.284	5.838	1.762	3.103	11.825	29.583	0.148
	60	82.848	-2.224	10.487	-0.212	0.045	10.720	101.973	0.129
	90	87.346	-16.825	21.959	-0.766	0.587	27.664	127.459	0.317
I_B	1	69.511	35.284	-3.085	-11.435	130.768	35.419	355.003	0.509
	30	71.317	33.257	3.401	9.779	95.633	33.430	5.839	0.469
	60	76.015	21.317	10.837	1.967	3.869	23.913	26.947	0.315
	90	75.315	20.882	13.549	1.541	2.375	24.892	32.977	0.330
II	1	69.866	-22.216	-18.370	1.209	1.462	28.828	230.413	0.413
	30	83.528	25.637	6.009	4.266	18.206	26.332	13.191	0.315
	60	85.774	17.350	9.644	1.798	3.236	19.850	29.067	0.231
	90	86.822	19.156	11.556	1.657	2.747	22.371	31.101	0.258

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Also, an important hypsochromic effect can be observed at sample I_B in first month specially (with complementary wavelenghts values around 497–498 nm). On the other hand, table 3 shows the evolution of the hue angle whilst maturation wine samples as a numerical expression for qualitative measurement of chromaticity. In most cases, a slight increase from blue hues to red or orange - yellow hues exists in first month. The saturation, s^* is major for I_B sample.

Table 4 shows the regression equations for lightness with each chromatic parameter from the first day of the experiment.

Table 4. The regression equations for lightness with each chromatic parameter studied

Sample	Parameter	Equation	Correlation, r
I_A	a^*	$L = 82.04 - 0.31 \cdot a^*$	- 0.965
	b^*	$L = 77.47 + 0.46 \cdot b^*$	0.995
	C^*	$L = 76.15 + 0.41 \cdot C^*$	0.914
I_B	a^*	$L = 84.21 - 0.4 \cdot a^*$	- 0.985
	b^*	$L = 70.56 + 0.4 \cdot b^*$	0.964
	C^*	$L = 88.69 - 0.53 \cdot C^*$	- 0.995
II	a^*	$L = 78.08 + 0.34 \cdot a^*$	0.947
	b^*	$L = 80.25 + 0.57 \cdot b^*$	0.999
	C^*	$L = 120.86 - 1.62 \cdot C^*$	- 0.822

$p < 0.05$; regression: 95%

The redness parameter of CIELAB system is the parameter with the highest correlation. This parameter also had the highest coefficient of variation. Therefore, redness appears to be the most sensitive parameter for panellists. Also it is remarked the fact that is a low correlation between lightness and C* parameter for the wine sample from Bujor Hills. The diagram of L parameter vs. the panellists scores was somehow similar to the lightness variations from table 3.

Of course, the research carried out could not aboard all aspects concerning red wine production, limiting itself only at those who have a more important role and could have been studied in the offered conditions. In the future we intend to extend this study on a longer period of maturation time.

4. Conclusions

This study presented a good objective evaluation of colour function in red wines by using simpler methods and tristimulus CIE parameters and their correlation to pigmentation in wines.

While wine is maturating color intensity decreases and tint increases. The evolution of wine color in maturing process depends on their composition, sort and aplied technology.

The greater uniformity of the colour spaces CIELAB offers more good chromatic characterisations of the wines studied than the CIE Yxy system.

Under organoleptic aspect, studied wine sorts are intensely colored and will gain a lot from one long maturing. Wines from Tighina and Bujor Hills missed in the process of maturation a reddish tint, and a red-orange tint and both types of red wines underlined the fact that they lacked the freshness and fructosity.

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