

ASPECTS CONCERNING THE EVOLUTION IN TIME OF CHROMATIC PARAMETERS IN SOME RED WINES

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ABSTRACT - This study presents the evolution in time of the chromatic parameters (L, a, b, C, H⁰) over 24 months, as well as the variation of total phenolic compounds (anthocyanins) and the variation of the main colour characteristics (intensity and shade), correlated to the corresponding pH changes. Twelve red wines from four grape varieties (Cabernet Sauvignon, Merlot, Fetească neagră and Băbească neagră), cultivated in the Dealu Bujorului vineyard, Galați County, obtained by classical fermentation, rototanks and thermo-maceration, were studied. The wines were obtained in October 2005 at the pilot research station and were analysed in the same month, November, of the years 2005, 2006 and 2007. The analyses have shown a variation in time of the studied parameters, depending on the oenological potential of each variety and used technology. A change in this value was noticed mainly as a decrease of the total phenolic compounds (anthocyanins), correlated especially to the variation of the pH values. Data concerning the chromatic parameters of each wine allowed an objective appreciation of the red young wines colour and of their evolution in time (during 2 years).

Key words: red varieties, absorption spectrum, evolution, chromatic parameters

REZUMAT - Aspecte privind evoluția în timp a parametrilor cromatici la unele vinuri roșii. În lucrarea de față s-a urmărit evoluția în timp a parametrilor cromatici (L, a, b, C, H⁰) pe parcursul a 24 de luni, concomitent cu variația valorilor compuşilor fenolici totali (respectiv ale antocianilor) și a principalelor caracteristici de culoare (intensitate și nuanță), în corelație cu modificările corespunzătoare ale pH-ului. S-au studiat 12 vinuri roșii, obținute prin macerarea-fermentarea (sistem clasic, cisterne rotative, termomacerare) a strugurilor din patru

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soiuri negre (Cabernet Sauvignon, Merlot, Fetească neagră, Băbească neagră), cultivate în podgoria Dealu Bujorului, jud. Galați. Vinurile au fost obținute în luna octombrie 2005, în condiții de stație pilot, și au fost analizate în luna noiembrie din anii 2005, 2006 și 2007. Determinările au evidențiat o variație în timp a valorilor parametrilor studiați, dependentă de potențialul oenologic al fiecărui soi în parte și de tehnologia folosită, constatându-se modificări ale acestora, evidențiate, în special, prin scăderea conținutului de compuși fenolici totali (mai ales prin diminuarea antocianilor), corelate, în mare parte, cu variația valorilor pH-ului. Datele privind parametrii cromatici ai fiecărui vin în parte permit aprecierea obiectivă atât a culorii vinurilor roșii tinere, cât și pe parcursul evoluției acestora în timp, pe o perioadă de doi ani.

Cuvinte cheie: soiuri roșii, spectru de absorbție, evoluție, parametri cromatici

INTRODUCTION

The present wine investigations concerning the chemical nature of the chromatic compounds from red wines have shown that for the objective description of different wine types and of their differences, they should use the content in phenolic compounds (especially, of the anthocyanins) and the chromatic parameters.

This study is found within the European concerns in this field, by calculating the most important parameters for identifying the red varieties of *Vitis vinifera*, both as regards the health condition and solving the disputes between different partners.

In this paper, we have followed the evolution in time of the chromatic parameters (B , a , b , C , H^0) for 24 months, simultaneously to the variation in the values of total phenolic compounds (respectively, of the anthocyanins) and of the main colour characteristics (intensity and shade), correlated to the pH corresponding changes. This took place during the evolution of the analysed red wines, for two years, from their obtaining in November 2005 and during November 2006 and 2007.

MATERIALS AND METHODS

The investigations on the variation in time of the chromatic parameters (B , a , b , C , H^0) were conducted on 12 red wine samples, obtained by the technological variants of maceration-fermentation (classical systems, rototanks and thermo-maceration) of grapes from four black varieties (Cabernet Sauvignon, Merlot, Fetească neagră and Băbească neagră), cultivated in the Dealu Bujorului vineyard, Galați County, vintage of year 2005.

The analysed wines (samples 1÷12, according to data from Table 1) were obtained under conditions of a pilot station in October 2005, within the Oenological Research Centre of the Iași Branch of the Romanian Academy. Samples 1÷12 were preserved in glass containers of different sizes, for six months, then they were sulphitated with doses of 50 mg/L sulphur dioxide and bottled in bottles of 0.7 L.

Wines were analysed the same month, November, of years 2005, 2006 and 2007. The physical-chemical analyses (alcohol, total acidity, non-reducing sugars, non-reducing extract, pH, anthocyanins, total phenolic compounds, colour intensity and shade) were made

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according to the methods indicated by in force State and international standards (** 1988; *** 2005) or by literature (Bourzeix, 1976; Cotea, 1985; Cotea et al., 2002; Ribereau-Gayon et al., 1972; Rusu, 2006; Țârdea, 2007; Wittkowski, 1999).

The chromatic parameters of the wine sampled at the early wine drawing off, after one and two years, respectively, were calculated by the methods of CIE Lab 76 (Odăgeriu et al., 2000), according to the absorption spectrum registered for each sample. This was done with the SPECORD S200 spectrophotometer, coupled to a computer. Thus, the absorption spectrum was recorded automatically in a file. For minimising the analysis errors in the determination of absorbance, we have used optical way tanks, proper for each wine sample, respectively of 0.2 cm. Spectra were processed with a programme made by our research team, for getting chromatic parameters (**B**, **a**, **b**, **C**, **H°**), intensity of colour (**I**) and shade (**S**).

Based on the obtained results, we have also calculated the relative deviation (δ_r) in %, by which we have changed pH, content in phenolic compounds, chromatic characteristics and chromatic parameters of the wines studied during the two years of investigation.

RESULTS AND DISCUSSION

After two years since they were obtained (in November 2007), the main composition characteristics of the analysed wines (samples 1÷12) are shown in *Table 1*.

Table 1 – Main composition characteristics of the analysed wines

No.	Technological variant of maceration-fermentation	Alcohol (% vol.)	Total acidity (g/L C ₄ H ₆ O ₆)	pH	Reducing sugars (g/L)	Non-reducing extract (g/L)
CABERNET SAUVIGNON						
1	Classical system (V ₁₁)	12.25	6.66	3.57	2.16	22.14
2	Rototank (V ₁₂)	12.43	5.92	3.73	2.18	21.03
3	Thermo-maceration (V ₁₃)	14.20	4.08	4.03	2.65	23.35
MERLOT						
4	Classical system (V ₂₁)	13.17	6.03	3.57	2.52	23.28
5	Rototank (V ₂₂)	13.47	7.56	3.30	2.24	23.06
6	Thermo-maceration (V ₂₃)	14.77	5.61	3.75	2.52	24.03
FETEASCĂ NEAGRĂ						
7	Classical system (V ₃₁)	13.53	6.06	3.62	1.89	21.21
8	Rototank (V ₃₂)	13.62	6.05	3.56	1.67	21.32
9	Thermo-maceration (V ₃₃)	15.03	5.99	3.76	2.36	23.00
BĂBEASCĂ NEAGRĂ						
10	Classical system (V ₄₁)	13.00	7.35	3.58	2.02	20.73
11	Rototank (V ₄₂)	13.05	6.45	3.58	2.03	19.47
12	Thermo-maceration (V ₄₃)	13.45	4.95	3.74	2.05	21.15

Higher values than 11.00% vol. of the alcoholic concentration in all the analysed wines, corroborated to higher values than 19.00 g/L of the non-reducing extract, pointed out their framing within the category of high quality wines with controlled origin denomination (DOC), while some of them were wines with rating scales of quality (DOC-CMD).

Table 2 shows the variation in the content of total phenolic compounds of the chromatic characteristics and in pH of the analysed wines, for two years. Determinations pointed out a variation in time of the values of studied phenolic compounds, depending on the oenological potential of each variety and used technology. Thus, we found out specific modifications, pointed out by diminishing the content of total phenolic compounds and especially, of anthocyanins. At the same time, we noticed an evident increase in the colour intensity during the first year of evolution, although the literature (Bourzeix, 1976) showed a diminution in time. This could be explained by the fact that most of the anthocyanins, which value diminished, were blocked by sulphur dioxide or were degraded in the presence of oxygen, leading to the formation of colourless and yellow compounds, which resulted in the increase of the value of the colour intensity. This aspect may be due to the reactions of tannins (condensation, polymerization and oxidation), which led to the formation of compounds with similar influence on the intensity of colour. However, in the next year of evolution, we found a slight diminution in the colour intensity, as a result of some reactions between the compounds responsible of the colour in the reductive system, made by wine bottling.

Table 2 – Variation in the content of total phenolic compounds of chromatic characteristics and of pH in the analysed wines, for two years

Specification	M.U.	Technological variant								
		Classical system			Rototanks			Thermo-maceration		
Year		2005	2006	2007	2005	2006	2007	2005	2006	2007
CABERNET SAUVIGNON (samples V₁₁, V₁₂, V₁₃)										
Total phenolic compounds	g/L	2.62	2.25	2.12	2.79	2.41	2.23	3.95	3.64	3.44
	δ_r (%)	0.0	-14.1	-19.1	0.0	-13.6	-20.1	0.0	-7.8	-12.9
Anthocyanins	mg/L	707	336	209	662	289	103	736	434	238
	δ_r (%)	0.0	-52.5	-70.4	0.0	-56.3	-84.4	0.0	-41.0	-67.7
Colour intensity	1 cm	12.21	14.94	14.85	10.61	14.47	14.60	12.04	18.78	17.92
	δ_r (%)	0.0	22.4	21.7	0.0	36.4	37.7	0.0	56.0	48.8
Shade (A₄₂₀/A₅₂₀)		0.37	0.53	0.62	0.39	0.65	0.74	0.49	0.70	0.79
	δ_r (%)	0.0	41.9	66.0	0.0	64.7	87.5	0.0	42.2	60.4

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Specification	M.U.	Technological variant								
		Classical system			Rototanks			Thermo-maceration		
Year		2005	2006	2007	2005	2006	2007	2005	2006	2007
pH		3.46	3.51	3.57	3.57	3.60	3.73	3.87	3.92	4.03
	δ_r (%)	0.0	1.4	3.2	0.0	0.8	4.4	0.0	1.3	4.0
MERLOT (samples V₂₁, V₂₂, V₂₃)										
Total phenolic compounds	g/L	2.20	1.85	1.64	2.62	2.19	2.08	3.43	3.11	3.06
	δ_r (%)	0.0	-15.9	-25.5	0.0	-16.4	-20.6	0.0	-9.3	-10.8
Anthocyanins	mg/L	640	265	110	632	219	98	591	266	243
	δ_r (%)	0.0	-58.6	-82.8	0.0	-65.3	-84.5	0.0	-55.0	-58.9
Colour intensity	1 cm	10.57	11.34	15.87	11.28	17.00	14.29	9.89	16.40	13.92
	δ_r (%)	0.0	7.3	50.1	0.0	50.8	26.7	0.0	65.8	40.7
Shade (A ₄₂₀ /A ₅₂₀)		0.36	0.47	0.64	0.36	0.55	0.60	0.45	0.69	0.72
	δ_r (%)	0.0	28.9	75.5	0.0	54.4	68.5	0.0	54.2	60.9
pH		3.37	3.50	3.57	3.33	3.36	3.30	3.54	3.58	3.75
	δ_r (%)	0.0	3.9	6.0	0.0	0.9	-0.9	0.0	1.1	5.8
FETEASCĂ NEAGRĂ (samples V₃₁, V₃₂, V₃₃)										
Total phenolic compounds	g/L	2.25	1.97	1.82	2.20	1.88	1.81	3.16	3.00	2.87
	δ_r (%)	0.0	-12.4	-19.1	0.0	-14.5	-17.7	0.0	-5.1	-9.2
Anthocyanins	mg/L	525	233	80	556	224	153	533	373	245
	δ_r (%)	0.0	-55.6	-84.8	0.0	-59.7	-72.5	0.0	-30.0	-54.0
Colour intensity	1 cm	7.72	11.56	10.92	8.40	12.49	11.19	9.89	14.21	13.10
	δ_r (%)	0.0	49.7	41.5	0.0	48.7	33.2	0.0	43.7	32.5
Shade (A ₄₂₀ /A ₅₂₀)		0.41	0.58	0.63	0.40	0.62	0.68	0.45	0.62	0.67
	δ_r (%)	0.0	41.5	53.7	0.0	55.0	70.0	0.0	37.8	48.9
pH		3.51	3.52	3.62	3.45	3.51	3.56	3.58	3.60	3.76
	δ_r (%)	0.0	0.3	3.0	0.0	1.7	3.2	0.0	0.6	5.0
BĂBEASCĂ NEAGRĂ (samples V₄₁, V₄₂, V₄₃)										
Total phenolic compounds	g/L	1.95	1.73	1.58	1.80	1.55	1.46	2.89	2.63	2.55
	δ_r (%)	0.0	-11.3	-19.0	0.0	-13.9	-18.9	0.0	-9.0	-11.8
Anthocyanins	mg/L	452	244	92	454	213	130	515	263	177
	δ_r (%)	0.0	-46.0	-79.6	0.0	-53.1	-71.4	0.0	-48.9	-65.6

Specification	M.U.	Technological variant								
		Classical system			Rototanks			Thermo-maceration		
Year		2005	2006	2007	2005	2006	2007	2005	2006	2007
Colour intensity	1 cm	6.68	12.41	11.54	5.93	9.08	8.04	7.81	11.86	9.37
	$\bar{d}_r$ (%)	0.0	85.8	72.8	0.0	53.1	35.6	0.0	51.9	20.0
Shade (A_{420}/A_{520})		0.45	0.67	0.69	0.41	0.63	0.73	0.48	0.67	0.72
	$\bar{d}_r$ (%)	0.0	48.9	53.3	0.0	53.7	78.0	0.0	39.6	50.0
pH		3.52	3.55	3.58	3.44	3.45	3.58	3.54	3.61	3.74
	$\bar{d}_r$ (%)	0.0	0.9	1.7	0.0	0.3	4.0	0.0	2.0	5.7

At the same time, we found out that most of the observations were correlated to the variation of pH values. It registered increasing values in time in most of the analysed wines, which might determine the modification of the chromatic characteristics (intensity and shade), as a result of the specific influence of pH on anthocyanins.

These assessments are, generally, true for all the analysed wines, obtained by the three technological variants (classical system, rototanks and thermo-maceration), from the four studied varieties. The differences concern especially the height of variations, according to the initial values of colour compounds of each wine. The two year-variation of the chromatic parameters in the analysed wine is shown in Table 3. The chromatic parameters are illustrated by brightness **B**, coordinates of colour **a** and **b**, chromaticity **C** and angle of shade **H°**.

Generally, there is a correlation between brightness and intensity of wine colour. Thus, in young wines (those analysed in November 2005), intensely coloured, due to their enrichment in phenolic compounds, the brightness is lower and, reversely, it is higher in less coloured wines (Odăgeriu et al., 2000). After one year and two years, respectively, it has diminished slightly, as a result of wine colour intensification, due to pH changes, caused by the diminution at certain proportions in the total acidity of the analysed wines.

The relatively high positive values of the parameter **a**, situated on the coordinate of red-green colours, show the prevalence of red shades against the green ones. We found a diminution in its value, because of the colour modification during the two years.

The chromatic parameter **b**, situated on the coordinate of blue-yellow colours, has shown a similar evolution to that of the parameter **a**. Because all the values of the chromatic parameter **b** were positive, the blue shades were prevalent against the yellow ones and, as a result of the diminution in the value of total phenolic compounds, they were enough coloured.

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The values of the chromaticity **C** from the analysed wines, being calculated according to the chromatic parameters **a** and **b**, corresponding to each wine, had similar evolutions to these. Thus, as concerns the wines analysed in 2007, we found that in low chromaticity wines, brightness diminished, while the high chromaticity wines were the most intensely coloured, as in most of the analysed samples.

The values of the colour shade (**H°**) in the analysed wines had similar evolutions to the other chromatic parameters, being descendant. Taking into account the value of the shade angle **H°** = 90° (determined in the same month, November, of years 2005, 2006 and 2007), corresponding to the colour of “pure yellow”, we noticed that the wines analysed with **H°** lower than 90° were perceived with “blue” shades. The bright red was more pronounced, as the angle of shade was closer to zero and, therefore, less influenced by yellow shades.

Table 3 – Variation of chromatic parameters in the analysed wines, for two years

Specification	M.U.	Technological variant								
		Classical system			Rototanks			Thermo-maceration		
Year		2005	2006	2007	2005	2006	2007	2005	2006	2007
CABERNET SAUVIGNON (samples V₁₁, V₁₂, V₁₃)										
B		16.40	8.37	7.60	17.98	7.80	6.15	9.87	3.28	3.02
	$\bar{\delta}_r$ (%)	0.0	-49.0	-53.7	0.0	-56.6	-65.8	0.0	-66.8	-69.4
a		48.83	38.56	37.45	50.6	37.83	34.63	40.20	23.07	21.17
	$\bar{\delta}_r$ (%)	0.0	-21.0	-23.3	0.0	-25.2	-31.6	0.0	-42.6	-47.3
b		27.82	14.42	13.10	29.93	13.44	10.60	16.81	5.65	5.21
	$\bar{\delta}_r$ (%)	0.0	-48.2	-52.9	0.0	-55.1	-64.6	0.0	-66.4	-69.0
C		56.20	41.17	39.67	58.79	40.14	36.22	43.58	23.75	21.81
	$\bar{\delta}_r$ (%)	0.0	-26.7	-29.4	0.0	-31.7	-38.4	0.0	-45.5	-50.0
H°		29.67	20.50	19.28	30.60	19.56	17.02	22.69	13.76	13.82
	$\bar{\delta}_r$ (%)	0.0	-30.9	-35.0	0.0	-36.1	-44.4	0.0	-39.3	-39.1
MERLOT (samples V₂₁, V₂₂, V₂₃)										
B		20.71	13.86	14.29	19.95	7.88	7.28	16.13	3.96	5.00
	$\bar{\delta}_r$ (%)	0.0	-33.1	-31.0	0.0	-60.5	-63.5	0.0	-75.5	-69.0
a		53.74	45.44	45.52	52.98	38.28	37.27	47.83	26.63	30.88
	$\bar{\delta}_r$ (%)	0.0	-15.4	-15.3	0.0	-27.7	-29.7	0.0	-44.3	-35.4
b		34.43	23.41	24.17	33.54	13.58	12.55	26.75	6.82	8.63
	$\bar{\delta}_r$ (%)	0.0	-32.0	-29.8	0.0	-59.5	-62.6	0.0	-74.5	-67.8
C		63.82	51.12	51.54	62.70	40.62	39.33	54.80	27.49	32.06
	$\bar{\delta}_r$ (%)	0.0	-19.9	-19.2	0.0	-35.2	-37.3	0.0	-49.8	-41.5
H°		32.65	27.26	27.97	32.34	19.54	18.61	29.22	14.37	15.61
	$\bar{\delta}_r$ (%)	0.0	-16.5	-14.3	0.0	-39.6	-42.4	0.0	-50.8	-46.6

Specification	M.U.	Technological variant								
		Classical system			Rototanks			Thermo-maceration		
Year		2005	2006	2007	2005	2006	2007	2005	2006	2007
FETEASCA NEAGRA (samples V₃₁, V₃₂, V₃₃)										
B		24.01	11.63	9.68	22.91	9.79	10.37	16.13	9.52	10.59
	$\bar{o}_r$ (%)	0.0	-51.5	-59.7	0.0	-57.3	-54.7	0.0	-41.0	-34.4
a		56.41	42.78	40.46	55.68	40.59	41.28	47.83	40.31	41.55
	$\bar{o}_r$ (%)	0.0	-24.2	-28.3	0.0	-27.1	-25.9	0.0	-15.7	-13.1
b		34.87	19.93	16.52	35.01	16.83	17.78	26.75	16.40	18.25
	$\bar{o}_r$ (%)	0.0	-42.8	-52.6	0.0	-51.9	-49.2	0.0	-38.7	-31.8
C		66.31	47.20	43.71	65.77	43.94	44.94	54.80	43.52	45.38
	$\bar{o}_r$ (%)	0.0	-28.8	-34.1	0.0	-33.2	-31.7	0.0	-20.6	-17.2
H⁰		29.30	24.98	22.21	32.16	22.52	23.31	29.22	22.14	23.71
	$\bar{o}_r$ (%)	0.0	-14.7	-24.2	0.0	-30.0	-27.5	0.0	-24.2	-18.9
BĂBEASCA NEAGRA (samples V₄₁, V₄₂, V₄₃)										
B		25.75	12.21	9.24	29.79	15.28	16.82	18.36	8.32	12.85
	$\bar{o}_r$ (%)	0.0	-52.6	-64.1	0.0	-48.7	-43.5	0.0	-54.7	-30.0
a		57.27	43.88	39.90	61.09	47.00	48.49	48.83	38.12	43.76
	$\bar{o}_r$ (%)	0.0	-23.4	-30.3	0.0	-23.1	-20.6	0.0	-21.9	-10.4
b		33.26	21.03	15.92	30.04	25.62	28.10	26.98	14.27	21.76
	$\bar{o}_r$ (%)	0.0	-36.8	-52.1	0.0	-14.7	-6.4	0.0	-47.1	-19.4
C		66.23	48.66	42.96	68.08	53.53	56.04	55.79	40.70	48.87
	$\bar{o}_r$ (%)	0.0	-26.5	-35.1	0.0	-21.4	-17.7	0.0	-27.0	-12.4
H⁰		30.15	25.61	21.75	26.18	28.60	30.09	28.92	20.53	26.44
	$\bar{o}_r$ (%)	0.0	-15.1	-27.9	0.0	9.2	14.9	0.0	-29.0	-8.6

CONCLUSIONS

Determinations have shown a variation in time of the values of studied parameters, depending on the oenological potential of each variety and of the used technology. We found modifications of values, pointed out by the diminution in the content of total phenolic compounds (especially, by the anthocyanins diminution), correlated to the pH variation.

These data are fit for all the analysed wines, obtained through the three technological variants (classical system, rototanks and thermo-maceration) from the four studied varieties. The differences concern especially the height of variations, which are according to the initial values of the colour compounds from each wine.

Data concerning the colour characteristics (chromatic parameters, intensity and shade), determined for each wine, allow us to make an objective estimate of

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the colour in young red wines and, implicitly, on their quality, during their evolution in time.

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