SPECTROPHOTOMETRIC CHARACTERIZATION OF RED WINE COLOR FROM THE VINEYARD REGION OF METOHIJA

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Abstract: Five types of red wine produced from the grape varieties from the Metohia region (vintage 2014) were characterized on the basis of their chromatic properties. The properties of bottled wines: Merlot, Vranac, Prokupac, Cabernet and Game were analyzed. Chromatic characteristics of these wines were observed four times during the year – spectrophotometer measurements were performed on wines aged 0, 4, 8 and 12 months. Intensity, hue and brilliance of color of these wines were determined (by the usual method of Glories). The amount of coloring matter was determined by the usual method of Durmishidze and the percentage of polymeric anthocyanins was calculated as well. Wine ageing decreased the color intensity while the color hue value increased. It was also found that contribution of wine color red pigment decreased with wine ageing, while the percentage of yellow pigment in wine increased. The total amount of colored substances in wines studied decreased with wine ageing, while the percentage of polymeric pigments in wine increased. This study presents the methodology for analyses of the chromatic characteristics, and explains the origin influence of wine on these properties. On the basis of these correlations the quality of red wine can be established.

Keywords: wines, chromaticity, pigments, red wines.

Introduction

Present-day studies point to the fact that of all the foods and beverages that people consume wine is the most important source of substances playing a protective role against cardiovascular diseases, cancer and neurodegenerative diseases (Fuhrman et al., 1995; Wood et al., 1982; Okuda et al., 1992). The protective role comes from components derived from non-alcoholic wine comprising the wine polyphenols, tannins and anthocyanins in particular, which have a high antioxidant activity. Numerous studies have shown that geographical
origin and grape varieties have a significant effect on the antioxidant and also on the red wine color (Budić-Leto et al., 2003; Kovač et al., 1995).

Phenolic compounds are a widespread group of plant metabolites, which can be of a very simple structure, such as phenolic acids, or of a complex structure, i.e. polycondense compounds, such as proanthocyanidins (Lekuta et al., 2005).

Four main groups of phenol compounds include phenolic acids, flavonoids, anthocyanins and tannins. The flavonoids are yellow-hued derivatives of flavone, where R and R1 are substituents (Figure 1).

![Figure 1. Flavonoids.](image)

A related compound is the major red pigment in wine, malvidin-3-monoglucoside, and anthocyanin (Figure 2).

![Figure 2. Malvidin-3-monoglucoside.](image)
Spectrophotometric analysis of the red wine color

The spectrum of red wine has a maximum at 520 nm, due to anthocyanins and their flavylium combinations, and a minimum in the region of 420 nm. Color intensity and hue, as defined by Sudraud (1958), only take into account the contributions of red (520 nm) and yellow (420 nm) overall colors. Of course, the results of this partial analysis cannot claim to reflect the overall visual perception of a wine color. The current approach to color analysis in winemaking requires optical density measurements at 420 and 520 nm, with an additional measurement at 620 nm to include the blue component in young red wines, so called the Glories method (1984). These measurements are used to calculate the values employed to describe wine color.

Wine color intensity (I) is an amount of color. It varies greatly in different types of wine:

\[
I = A_{420} + A_{520} + A_{620}
\]  

Wine hue (T) indicates the development of a color towards orange. Young wines have a value on the order of 0.5–0.7 which increases throughout aging, reaching an upper limit of around 1.2–1.3.

\[
T = \frac{A_{520}}{A_{420}}
\]

Chromatic structure, i.e. the contribution (in percentage) for each of the three components of the total color:

\[
A_{420} (\%) = \frac{A_{420}}{I} \cdot 100
\]

\[
A_{520} (\%) = \frac{A_{520}}{I} \cdot 100
\]

\[
A_{620} (\%) = \frac{A_{620}}{I} \cdot 100
\]

The brilliance of red wines (d) is associated with the shape of the spectrum. When the wine is bright red, the maximum spectrum at 520 nm is narrow and well defined. On the other hand, the maximum of the spectrum is relatively broad and flattened when wine is deep red or brick red. This feature can be presented as follows:

\[
dA = \left(\frac{1}{\frac{d}{2A_{520}}}\right) \cdot 100
\]

Expected results are between 40 and 60 in young wines. A higher value indicates a dominance of red wine (Ribèreau-Gayon et al., 2006).
Spectrophotometric determination of the amount of coloring matters and the percentage of polymeric anthocyanins in red wine

Coloring matters of red grapes and wine are anthocyanins. They are among the most important plant pigments. The grape and wine anthocyanins are mostly in the form of glycosides. Grape variety, V. vinifera, is characterized mainly by the presence of monoglucoside. The most common anthocyanins in grapes and wine are malvidin, peonidin and cyanidine. In the pink wine, the colored matter content ranges from 50 to 100 mg/dm³, in normal-colored red wines from 100 to 200 mg/dm³, and in highly colored wines, it can occur in up to 500 mg/dm³.

Before the spectrophotometric measurement of the amount of colored substances in a solution is performed, it is necessary to determine the light wavelength to be used in the analysis. Experimentally, it has been found that in red wines the strongest absorbance of light of wavelengths is around 530 nm, therefore, in the spectrophotometric determination of the amount of colored substances in red wine, this light of wavelength is used (Blesić, 2006).

Among the numerous methods for the spectrophotometric determination of the content of colored substances in red wine, due to the simple execution and obtaining the results of satisfactory accuracy, the method Durmishidze (1958) has been used. This method is based on the spectrophotometric determination of transparency of the defined wine solution layer and on the basis of that, it leads to the indirect determination of the content of colored compounds using Durmishidze's table, which specifies the amount of colored substances (mg in 10 cm³ of wine, diluted according to the procedure by the author).

The determination of the percentage of polymer of anthocyanin is performed by chemical treatment of the analyzed wine by sulfur dioxide, by the Russo method (2011). Sulfur dioxide, a product of sodium metabisulfite, bleaches any monomeric anthocyanins. The residual color of the wine is derived from polymerized phenolic compounds, mostly from anthocyanins. The percentage of polymer of anthocyanin is calculated as the ratio of the absorbance obtained for the wine tested at 520 nm to the absorbance for the same wine treated with sulfur dioxide:

\[
P_A(\%) = \frac{A_{SO_2}}{A_{SO_2}} \cdot 100
\]

Material and Methods

In this study, we analyzed the red wine produced from the varieties of Metohija regions (vintage 2014). The properties of wines: Merlot, Vranac, Prokupac, Cabernet and Game were examined. Chromatic characteristics of these wines were analyzed four times during the year, and measurements were made on the wine aged 0, 4, 8 and 12 months. We considered a very young wine (zero
Spectrophotometric characterization of red wine color from the vineyard region of Metohia

months) the wine that was the first to be decanted and filtrated. This process enables the essential clarity of wine samples.

For spectrophotometric measurements, Spectrophotometer UV-9200 RAY LEIGH was used. The experimental part was structured into the following main parts:

- Analysis of the color of red wine (chromatic parameters);
- Determination of the amount of coloring matters and the percentage of polymeric anthocyanins in red wine.

Spectrophotometric analysis of the color of red wine

For this type of analysis, the Glories method was used. The spectrophotometer was equipped with the optical path length cuvettes of 1 mm, and included the possibility of reading the absorbance at light wavelengths at 420, 520 and 620 nm. The wine used for analysis must be completely clear. The intensity, hue and brilliance of tested red wines were determined spectrophotometrically by measuring the absorbance at 420, 520 and 620 nm. Distilled water was used as a blank solution.

Values of parameters of intensity and hue, as well as brilliance of wines were calculated according to the forms set out in the introductory section of this paper.

Spectrophotometric determination of the amount of coloring matters and the percentage of polymeric anthocyanins in red wine

For spectrophotometric determination of amounts of colored substances in red wine the method of Durmishidze can be used. Contents of colored matters in red wine were expressed in mg/dm³. Determination of the percentage of polymeric anthocyanins was performed by the Russo method.

Results and Discussion

The data presented in Table 1 show chromatic parameters of examined wines obtained by the Glories method. By the use of this method, apart from intensity, hue and brilliance of red wine, the contributions of each pigment (yellow, red and blue) to wine color were also determined.

The contribution of the red pigment was most pronounced in very young Vranac and Merlot wines (48.0% and 48.6%), while the lowest contribution was pronounced in 12-month-old Prokupac and Game wines (40.9% and 41.4%). It can be concluded that the percentage of red pigment in the color of wine increases with the aging (Birse, 2007; Harbertson and Spayd, 2006; Poiana et al., 2007). In contrast, the percentage share of the yellow pigment of wine decreased. The
participation of the blue pigment in wine color was by far the least attended, it ranged from 10.6% for the young Merlot wine to a maximum of 21.2% for the 12-month-old Prokupac wine. The share of the red pigment was predominant in all analyzed wines and ranges, depending on the type and age of the wine from 41.7% to 48.0%. The contribution of the yellow pigment to red wine color ranged from 36.1% to 42.3%, which is correlated with information that can be found in literature (Birse, 2007; Harbertson and Spayd, 2006; Poiana et al., 2007).

Table 1. Chromatic properties of red wine determined by the Glories method.

<table>
<thead>
<tr>
<th>Wine type</th>
<th>$A_{420}$</th>
<th>$A_{520}$</th>
<th>$A_{620}$</th>
<th>I.C</th>
<th>T</th>
<th>dA (%)</th>
<th>% of yellow pigments</th>
<th>% of red pigments</th>
<th>% of blue pigments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Merlot 0</td>
<td>0.93</td>
<td>1.09</td>
<td>0.24</td>
<td>2.26</td>
<td>0.86</td>
<td>45.9</td>
<td>41.3</td>
<td>48.0</td>
<td>10.6</td>
</tr>
<tr>
<td>Merlot 4</td>
<td>0.93</td>
<td>1.06</td>
<td>0.24</td>
<td>2.23</td>
<td>0.88</td>
<td>44.9</td>
<td>41.6</td>
<td>47.6</td>
<td>10.8</td>
</tr>
<tr>
<td>Merlot 8</td>
<td>0.93</td>
<td>1.05</td>
<td>0.24</td>
<td>2.23</td>
<td>0.89</td>
<td>43.9</td>
<td>41.8</td>
<td>47.1</td>
<td>11.0</td>
</tr>
<tr>
<td>Merlot 12</td>
<td>0.94</td>
<td>1.03</td>
<td>0.25</td>
<td>2.22</td>
<td>0.91</td>
<td>42.3</td>
<td>42.3</td>
<td>46.4</td>
<td>11.3</td>
</tr>
<tr>
<td>Vranac 0</td>
<td>0.88</td>
<td>1.09</td>
<td>0.27</td>
<td>2.24</td>
<td>0.81</td>
<td>47.1</td>
<td>39.4</td>
<td>48.6</td>
<td>11.9</td>
</tr>
<tr>
<td>Vranac 4</td>
<td>0.89</td>
<td>1.07</td>
<td>0.27</td>
<td>2.23</td>
<td>0.83</td>
<td>45.6</td>
<td>39.9</td>
<td>47.9</td>
<td>12.2</td>
</tr>
<tr>
<td>Vranac 8</td>
<td>0.90</td>
<td>1.05</td>
<td>0.28</td>
<td>2.23</td>
<td>0.86</td>
<td>44.0</td>
<td>40.4</td>
<td>47.2</td>
<td>12.4</td>
</tr>
<tr>
<td>Vranac 12</td>
<td>0.92</td>
<td>1.03</td>
<td>0.28</td>
<td>2.23</td>
<td>0.89</td>
<td>41.7</td>
<td>41.1</td>
<td>46.2</td>
<td>12.7</td>
</tr>
<tr>
<td>Prokup 0</td>
<td>0.42</td>
<td>0.52</td>
<td>0.27</td>
<td>1.21</td>
<td>0.81</td>
<td>37.5</td>
<td>36.1</td>
<td>44.5</td>
<td>19.4</td>
</tr>
<tr>
<td>Prokup 4</td>
<td>0.48</td>
<td>0.50</td>
<td>0.23</td>
<td>1.21</td>
<td>0.96</td>
<td>34.2</td>
<td>36.9</td>
<td>43.2</td>
<td>19.9</td>
</tr>
<tr>
<td>Prokup 8</td>
<td>0.43</td>
<td>0.48</td>
<td>0.24</td>
<td>1.15</td>
<td>0.90</td>
<td>30.0</td>
<td>37.5</td>
<td>41.7</td>
<td>20.8</td>
</tr>
<tr>
<td>Prokup 12</td>
<td>0.47</td>
<td>0.47</td>
<td>0.24</td>
<td>1.18</td>
<td>1.00</td>
<td>27.7</td>
<td>37.9</td>
<td>40.9</td>
<td>21.2</td>
</tr>
<tr>
<td>Cabernet 0</td>
<td>0.66</td>
<td>0.78</td>
<td>0.23</td>
<td>1.67</td>
<td>0.85</td>
<td>42.8</td>
<td>39.6</td>
<td>46.5</td>
<td>13.9</td>
</tr>
<tr>
<td>Cabernet 4</td>
<td>0.68</td>
<td>0.76</td>
<td>0.23</td>
<td>1.67</td>
<td>0.90</td>
<td>39.7</td>
<td>40.6</td>
<td>45.3</td>
<td>14.0</td>
</tr>
<tr>
<td>Cabernet 8</td>
<td>0.69</td>
<td>0.74</td>
<td>0.24</td>
<td>1.67</td>
<td>0.93</td>
<td>37.2</td>
<td>41.3</td>
<td>44.3</td>
<td>14.3</td>
</tr>
<tr>
<td>Cabernet 12</td>
<td>0.70</td>
<td>0.71</td>
<td>0.29</td>
<td>1.70</td>
<td>0.99</td>
<td>33.3</td>
<td>42.2</td>
<td>42.8</td>
<td>14.9</td>
</tr>
<tr>
<td>Game 0</td>
<td>0.60</td>
<td>0.72</td>
<td>0.30</td>
<td>1.62</td>
<td>0.83</td>
<td>37.7</td>
<td>36.9</td>
<td>44.6</td>
<td>18.5</td>
</tr>
<tr>
<td>Game 4</td>
<td>0.61</td>
<td>0.70</td>
<td>0.30</td>
<td>1.61</td>
<td>0.87</td>
<td>34.8</td>
<td>37.7</td>
<td>43.4</td>
<td>18.8</td>
</tr>
<tr>
<td>Game 8</td>
<td>0.62</td>
<td>0.68</td>
<td>0.31</td>
<td>1.61</td>
<td>0.91</td>
<td>31.8</td>
<td>38.5</td>
<td>42.3</td>
<td>19.2</td>
</tr>
<tr>
<td>Game 12</td>
<td>0.62</td>
<td>0.66</td>
<td>0.31</td>
<td>1.59</td>
<td>0.94</td>
<td>29.3</td>
<td>38.8</td>
<td>41.4</td>
<td>19.7</td>
</tr>
</tbody>
</table>

The highest value of color intensity ($I$) was observed in young wines, especially in Merlot and Vranac (2.26 and 2.24) and the lowest value was recorded for Prokupac, aged 12 months – 1.18. With wine ageing the color intensity slightly
decreased. In contrast to the intensity, the value for the color hue (T) slightly increased with the process of the wine ageing (Birse, 2007; Harbertson and Spayd, 2006; Poiana et al., 2007). Thus, the maximum value for hue in a very young wine was found in Merlot – 0.86, and in 12-month-old wines it is was found in Cabernet – 0.99. Brilliance of wine also decreased with wine ageing and it was most pronounced in young Vranac – 47.1 and the lowest value was found in 12-month-old Prokupac – 27.7.

With wine ageing, the value measured at $\lambda = 520$ nm decreased, which was accompanied by an increase in the measured values of the wavelengths 420 nm and 620 nm. This can be explained by transition of monomeric anthocyanins into polymeric anthocyanins (Pasku, 2005).

Table 2 contains the values for the amount of colored substances in the red wines tested. With wine ageing, this value decreased, which was fully in line with the decline in the share of the red pigment in the color of wine. The highest value for the amount of colored matters was found in Merlot, in which the value of wine aging decreased from 309 mg/dm$^3$ to 226 mg/dm$^3$. The lowest value of this parameter was recorded for Game wine, and that value of wine aging decreased from 150 mg/dm$^3$ to only 70 mg/dm$^3$.

Table 2. Spectrophotometric determination of the amount of coloring matters in red wines tested.

<table>
<thead>
<tr>
<th></th>
<th>0 months</th>
<th>4 months</th>
<th>8 months</th>
<th>12 months</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T/%</td>
<td>Xa mg/dm$^3$</td>
<td>T/%</td>
<td>Xa mg/dm$^3$</td>
</tr>
<tr>
<td>M$^1$</td>
<td>8.3</td>
<td>0.155</td>
<td>309</td>
<td>10.30</td>
</tr>
<tr>
<td>V$^2$</td>
<td>10.2</td>
<td>0.138</td>
<td>276</td>
<td>12.10</td>
</tr>
<tr>
<td>P$^3$</td>
<td>26.5</td>
<td>0.080</td>
<td>160</td>
<td>32.50</td>
</tr>
<tr>
<td>C$^4$</td>
<td>11.8</td>
<td>0.139</td>
<td>278</td>
<td>15.50</td>
</tr>
<tr>
<td>G$^5$</td>
<td>28.1</td>
<td>0.075</td>
<td>150</td>
<td>34.10</td>
</tr>
</tbody>
</table>

$^1$M – Merlot, $^2$V – Vranac, $^3$P – Prokupac, $^4$C – Cabernet, $^5$G – Game, $^X$ – Durm.

In Table 3, the values for the percentage of polymeric anthocyanins in the wines tested are given. These values increased with wine ageing. Thus, the lowest percentage of polymeric anthocyanins was found in the young Merlot wine, 42.00%. With the ageing of this wine, that percentage increased to 62.00%, for the wine aged 12 months. The highest percentage of polymeric anthocyanins was found in the wine variety Cabernet and it ranged from 64.42% for a very young wine to 84.82% for the wine aged 12 months.
Table 3. Percentage of anthocyanins in red wines tested.

<table>
<thead>
<tr>
<th></th>
<th>Merlot</th>
<th>Vranac</th>
<th>Prokupac</th>
<th>Cabernet</th>
<th>Game</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 months</td>
<td>42.00</td>
<td>55.80</td>
<td>46.33</td>
<td>64.42</td>
<td>60.30</td>
</tr>
<tr>
<td>4 months</td>
<td>45.67</td>
<td>60.75</td>
<td>50.16</td>
<td>70.12</td>
<td>67.00</td>
</tr>
<tr>
<td>8 months</td>
<td>53.70</td>
<td>67.70</td>
<td>57.82</td>
<td>77.31</td>
<td>74.40</td>
</tr>
<tr>
<td>12 months</td>
<td>62.00</td>
<td>72.50</td>
<td>64.42</td>
<td>84.82</td>
<td>79.50</td>
</tr>
</tbody>
</table>

From the data shown in Tables 1, 2 and 3, it can be concluded that the aging of the wine is characterized by its chromatic change in the structure – it leads to the stabilization of color. The percentage of polymeric pigments in the color of wine increased by the aging process of wine. Namely, in this process the monomeric anthocyanins turn into polymeric anthocyanins with different molecular mass. In practice, this phenomenon of color evolution of red wine is called “wine ageing”. Stabilization of wine color is attributed to the reduction of participation of monomeric and copigmented anthocyanins in the wine content and the formation of combinations of tannins and anthocyanins – polymeric pigments which are characterized by red color. These polymeric pigments are highly stable compounds responsible for the color of old, red wine. Copigmented anthocyanins are complex compounds which result from the reaction between anthocyanins and copigmented molecules.

Conclusion

The wine ageing process affected the structure of the wine color. The percentage of the red pigment decreased with the aging process of wine while the participation of yellow hue increased for all red wines tested. The value of the color intensity of the wine was decreased by wine ageing in contrast to the values for the color hue of wine, which increased with the wine ageing. Most wine color intensity values were found in the young wines of Merlot and Vranac, 2.26 and 2.24, respectively. The lowest value for the wine hue was found in the young Prokupac wine – 0.81. The total amount of colored matters in studied wines decreased with wine ageing. The highest value for this parameter was found in the young Merlot wine – 309, while the lowest value was found in the 12-month-old Game wine – 70. The percentage of polymeric anthocyanins increased with wine ageing and its highest value was reached in the 12-month-old Cabernet wine – 84.82.
References


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SPEKTROFOTOMETRIJSKA KARAKTERIZACIJA BOJE CRVENIH VINA METOHIJSKOG REGIONA

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Rezime


Ključne reči: vina, obojenost, pigmenti, crvena vina.


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