CHANGES IN CIELAB CHROMATIC PROPERTIES OF WHITE WINES WITH MODELED HIGH CONTENTS OF SULFUR DIOXIDE

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Summary

Using the CIELAB method, the influence of extremely high doses of sulfur dioxide (from about 300 to about 1200 mg/L) in experimental-model white wines prepared from 31 samples of white wines from the Western Balkan region on changes in the chromatic properties of the wine was investigated. By spectrophotometric measurements and calculations, the values of the CIELAB indicators L* (clarity), a* (color along the red-green axis), b* (color along the yellow-blue axis) and ΔE* (overall colorimetric difference between the two wines) were determined. In the analyzed basic wines, the contents of free and total sulfur dioxide were found to be below the legally prescribed maximum concentrations in wines that are on the market. Changes in the values of indicators L*, a* and b* did not follow linear increases in sulfur dioxide content in experimental-model wines. However, on average for all wines, with increases in the content of sulfur dioxide in the specified range, there was an increase in the value of L* by about 1.6 units, a shift in the value of a* by about 1.5 units in a greener direction, and a shift in the value of b* in the direction of less yellow by about 2.3. Setting the value $\Delta E \geq 2$ as a difference in the color of the wine that could be determined visually, it was found that the modeled strong increase in the content of sulfur dioxide in the wines led to a significant change in color in about 65% of the analyzed wines. The predominant contribution to presumably visible changes in colors of the modeled wine came from changes in the value of the parameter b*. Bearing in mind the significant changes in the color of white wines noted in this research at the first model increase in sulfur dioxide content (by 200 mg/L), it would be useful to investigate changes in the color of white wines at different thresholds of increasing sulfur dioxide content up to this level.

Key words: *white wine, sulfur dioxide, CIELAB, chromatic characteristics of wine*

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INTRODUCTION

Due to its antioxidant and antimicrobial properties, sulfur dioxide is probably among the oldest, and certainly among the longest-lived enological agents. Although due to its proven negative effects on the health of consumers, as well as on some organoleptic properties of wine, its contents in the wines that are on the market are legally limited, wine production is still hard to imagine without its use. Legal regulations on wine reduce its permitted doses in winemaking over time, but the use of sulfur dioxide is allowed with slightly stricter restrictions even in the production of organic wines in the European Union (Regulation /EU/ 2021/1165). Therefore, sulfur dioxide will probably be an irreplaceable oenological agent for a long time to come.

Research on wine color has been and remains at the top of research interests, both because of the importance of color for the consumer's perception of wine, but also because of the challenging nature of the wine color phenomenon. In addition to other unwanted effects of sulfur dioxide, the fading effects of sulfur dioxide on the color of red wines that occur due to the binding of sulfur dioxide with anthocyanin structures, with the consequent changes in the chromatic properties of these structures, have been clarified in theory and are known in practice. The characterization and objectification of the color of primarily of red wines using instrumental (basically spectrophotometric methods) has long been performed by calculating the intensity (CI) and hue – tone (T) indicators of the color, promoted by French researchers in the middle of the 20th century. By promoting the so-called "CIELAB color space" by the International Commission on Illumination in 1976, wine color researchers received a new and relatively powerful tool for the objective characterization of wine color. The application of CIELAB in wine color analysis is promoted by a series of articles from the mid-nineties (among others: Ayala *et al*., 1997; Ayala *et al*., 1997a; Ayala *et al*., 1999; Pérez - Caballero *et al*., 2003). With its resolution of 2006, the International Organization for Vine and Wine (OIV) officially recommends a method for determining the chromatic characteristics of wines according to CIELAB (Method OIV-MA-AS2-11). Even before it was officially recommended by the OIV, researchers used the CIELAB based methods, but CIELAB significantly greater application occurred after it was made official. In addition to research related to the objective characterization of wine color, including research into the relationship between objectively (CIELAB) characterized color and its visual perception by human vision (e.g. Martínez *et al*., 2001, Huertas *et al*., 2003; Gamasa *et al*., 2009), researchers extend the application of the CIELAB method to studies of the contribution and role of a number of wine constituents on the expression of their colors (Han *et al*., 2008; González - Neves *et al*., 2010; Morina and Kongoli, 2012; Cucciniello *et al*., 2021). The CIELAB method is also recommended for quick, routine color analysis of red wines under production conditions (Pérez - Magarinõ, González - Sanjosé, 2003; Esparza *et al*., 2009). However, so far, a significantly larger number of studies have been carried out and published using the CIELAB method in the analysis of the color of red wines, than in the analysis of the color of white wines. To some extent surprisingly, there are few studies of the influence of oenological tools and procedures on the otherwise sensitive color of white wines. Among these studies, the investigation of the influences of chitin and chitosan (Spagna *et al*., 1996), filtration (Blesić *et al*., 2013), glutathione and ascorbic acid (Antoce *et al*., 2016), and wood chips (Delia *et al*., 2017) on changes in the color of white wines characterized by CIELAB chromatic indicators would be mentioned.

The aim of this research was to examine the potential influence of extremely high doses of sulfur dioxide in experimental-model white wines from the Western Balkans region on changes in their chromatic properties using the CIELAB method.

MATERIALS AND METHODS

The research materials were 31 dry white wines whose samples were taken from retail and private wine collections in Zenica and Sarajevo, Bosnia and Herzegovina. The basic data on the wines used in this research are given in Table 1.

Table 1. Basic data on the wines used as the research materials

Wine sample	Country of origin	Declared quality category	Year of harvest or packaging	Bottle volume (L)	Alcohol (% vol.)
1	Bosnia and Herzegovina	Premium	2007	0.75	12,5
2	Bosnia and Herzegovina	Premium	2020	0.75	13,0
3	Croatia	Premium	2009	0.75	13,4
4	Croatia	Premium	1999	0.75	13,1
5	Montenegro	Premium	2006	0.75	13,0
6	Bosnia and Herzegovina	Quality wine	2020	1	12,5
7	Bosnia and Herzegovina	Quality wine	2012	0.75	11,5
8	Bosnia and Herzegovina	Quality wine	2020	1	12,5
9	North Macedonia	Quality wine	2020	0.75	12,5
10	Croatia	Quality wine	2020	1	12,5
11	Bosnia and Herzegovina	Quality wine	2020	1	12,5
12	Bosnia and Herzegovina	Table wine	2020	1	12,0
13	Bosnia and Herzegovina	Table wine	2020	0.75	11,5
14	Bosnia and Herzegovina	Table wine	2020	0.75	13,0
15	Bosnia and Herzegovina	Table wine	2020	1	10,5
16	Serbia	Table wine	2021	1	11,0
17	Montenegro	Table wine	2014	1	11,5
18	Bosnia and Herzegovina	Table wine	2020	0.75	12,5
19	Bosnia and Herzegovina	Table wine	2018	0.75	13,0
21	Bosnia and Herzegovina	Table wine	2021	1	11,0
22	Bosnia and Herzegovina	Premium	2017	0.75	13,5
23	Montenegro	Quality wine	2019	1	12,5
24	Bosnia and Herzegovina	Quality wine	2018	1	12,0
25	Bosnia and Herzegovina	Table wine	2018	1	11,0
26	Bosnia and Herzegovina	Quality wine	2017	0.75	12,5
27	Serbia	Table wine	2019	1	11,5
28	Croatia	Quality wine	2011	0.75	12,7
29	North Macedonia	Quality wine	2021	0.75	12,5

Wine sample	Country of origin	Declared quality category	Year of harvest or packaging	Bottle volume (L)	Alcohol (% vol.)
30	Serbia	Table wine	2014	0.75	11,5
31	Bosnia and Herzegovina	Premium	2007	0.75	12,0
32	Serbia	Table wine	2020	1	10,5

The experiment plan involved increasing the content of total sulfur dioxide in wines to high and extremely high concentrations with the aim of determining the possible influence of increased concentrations of sulfur dioxide on the chromatic properties of white wines. Increases in the concentration of total sulfur dioxide in the model wines were, with the necessary calculations, made by adding a 20% potassium metabisulfite solution. High or very high doses of sulfur dioxide were added to total sulfur dioxide content in the basic wines (Table 2), as follows: 200 mg/L (Mod. A), 500 mg/L (Mod. B), 800 mg/L (Mod. C) and 1100 mg/L (Mod. D) of sulfur dioxide. In this way, model wines were obtained with total sulfur dioxide content (sulfur dioxide already contained in the wines and sulfur dioxide added to the wines) from about an average of 300 mg/L (Mod. A) to about an average of 1200 mg/L (Mod. D).

The contents of free and total sulfur dioxide in the analyzed white wines were determined by the iodometric Ripper method (Petrović, 2022). The method is quick and easy to implement, although today it is argued that it does not always give the most accurate results, especially when measuring the content of sulfur dioxide in red wines (Jenkins *et al.*, 2020).

The chromatic characteristics of the wine were determined according to the OIV OIV-MA-AS2-11 method. Optical density measurements at the wavelengths required by the method (450, 520, 570 and 630 nm) were performed on a Biochrom Libra S50 spectrophotometer (Biochrom US 84, Holliston, MA, USA), using a glass cuvette with an optical path length of 10 mm. The values of the CIELAB parameters L*, a* and b* were obtained from the measured absorbances, using the MSCV® software (Grupo de Color, Universidad de la Rioja – Universidad de Zaragoza). The values of ΔE* indicators (overall colorimetric difference between two wines) are calculated from the values of L*, a* and b*, according to the function given in the method OIV-MA-AS2-11: $\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$.

RESULTS AND DISCUSSION

Contents of total and free sulfur dioxide in basic wines

Table 2 lists the measured contents of free and total sulfur dioxide in 31 analyzed wines. According to the data from Table 2, in the 31 analyzed wines, the determined contents of total sulfur dioxide were from a minimum of 32 mg/L (wine 4) to a maximum of 192 mg/L (wine 19). The contents of total sulfur dioxide in all wines were below 200 mg/L, which is the maximum allowed content of total sulfur dioxide that can be found in wines that are on the market (Regulation /EU/ 2019/934; Pravilnik o kvalitetu vina, Službene novine Federacije BiH, 14/17). Observed according to the countries of origin of the wines, on average, the highest content of total sulfur dioxide was found in wines from Bosnia and Herzegovina (113 mg/L). It was followed by wines from Serbia (average 108 mg/L), then North Macedonia and Montenegro (94 mg/L) and wines from Croatia with, within these frameworks, the lowest average content of total sulfur dioxide (84 mg/L). Although among those analyzed there were wines with, one could say, critically high concentrations of total sulfur dioxide (192 mg/L, wine 19; 166 mg/L, wine 25; 165 mg/L, wine 18), overall observed, measured contents of total sulfur dioxide in the analyzed wines did not pose a danger to the health of their consumers.

Table 2. Contents of total and free sulfur dioxide (mg/L) in the analyzed wines

Wine	Total sulfur dioxide	Free sulfur dioxide	Wine	Total sulfur dioxide	Free sulfur dioxide
1	56	12	17	122	12
2	120	24	18	165	5
3	108	21	19	192	24
4	32	28	21	82	22
5	65	12	22	88	12
6	111	12	23	95	32
7	157	8	24	154	26
8	109	6	25	166	27
9	79	17	26	84	12
10	42	5	27	142	13
11	78	14	28	156	22
12	90	14	29	110	37
13	93	3	30	76	10
14	105	18	31	41	5
15	148	5	32	72	23
16	140	10			
Average (all wines)				**106**	**16**

The regulations of the European Union and the regulations of Bosnia and Herzegovina do not require the maximum allowed concentration of free sulfur dioxide in wines that are in market circulation. However, the contents of free sulfur dioxide determined in all analyzed wines are below the previously legally required maximum content of free sulfur dioxide in wine of 40 mg/l in Bosnia and Herzegovina.

Changes in the chromatic characteristics of wines with increased sulfur dioxide content

Table 3 presents the values of measured and calculated values of CIELAB parameters (L, a*, b*) in all analyzed basic and model wines with increased contents of total sulfur dioxide.

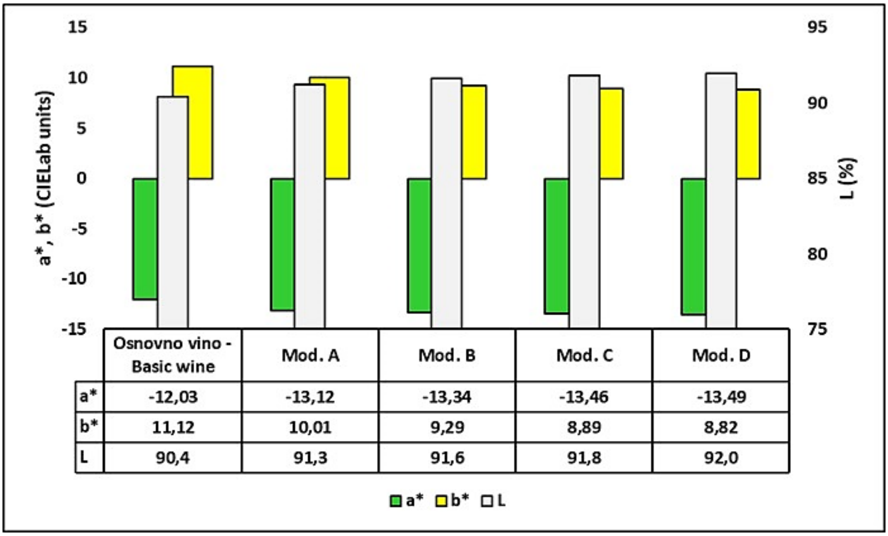
Table 3. Calculated values of CIELAB parameters L, a* and b* for basic and model wines

Wine sample	Basic wine			Mod. A			Mod. B			Mod. C			Mod. D		
	L	a*	b*	L	a*	b*	L	a*	b*	L	a*	b*	L	a*	b*
1	67.5	-13.92	25.80	68.6	-16.42	23.98	70.8	-18.16	23.02	73.1	-19.52	22.47	73.3	-20.75	21.56
2	93.9	-2.11	6.37	93.6	-2.22	6.06	94.2	-2.83	5.76	93.8	-2.37	5.35	93.7	-2.42	6.18
3	94.1	-2.66	6.33	94.8	-2.80	5.46	94.1	-2.94	6.29	94.8	-2.99	5.85	94.3	-3.41	5.27
4	73.4	-22.15	26.51	72.6	-28.05	25.94	73.5	-27.59	25.94	74.8	-28.51	24.23	74.8	-28.05	23.33
5	84.0	-31.09	3.69	84.9	-32.78	3.36	85.7	-33.45	3.21	85.3	-33.46	3.21	85.6	-33.37	3.19
6	94.3	-1.14	7.80	93.5	-1.77	7.04	94.3	-2.23	7.06	93.4	-2.62	6.99	94.4	-2.49	6.93
7	84.7	-31.76	3.43	85.3	-32.25	3.12	85.4	-32.96	1.67	85.1	-32.39	0.54	85.9	-32.77	0.42
8	95.6	-11.08	10.63	95.7	-11.14	10.15	95.9	-11.18	9.45	96.0	-11.29	9.16	95.8	-11.06	8.99
9	93.9	-1.13	6.25	93.5	-1.77	6.00	93.9	-1.60	5.91	93.9	-2.05	5.68	94.3	-2.10	6.01
10	82.0	-31.04	8.67	82.5	-31.88	8.22	82.7	-30.14	6.54	82.9	-31.38	5.66	82.8	-31.93	7.23
11	93.8	-1.36	5.98	93.8	-1.76	6.78	93.9	-1.90	5.74	93.9	-2.01	5.78	93.9	-2.14	6.40
12	96.1	-11.09	9.13	96.8	-11.73	9.51	96.8	-12.12	5.46	98.3	-12.51	5.07	98.8	-12.48	5.45
13	95.7	-8.65	5.16	95.8	-9.18	3.78	95.9	-9.29	3.81	95.9	-9.31	3.75	95.9	-9.32	3.90
14	93.1	-11.40	11.12	93.3	-11.58	7.16	95.5	-12.23	10.27	96.3	-11.10	8.26	98.7	-11.13	6.56
15	95.8	-11.38	10.39	96.0	-12.55	10.85	96.0	-12.58	9.56	96.1	-12.65	9.24	96.1	-12.27	6.83
16	95.7	-9.15	12.93	98.7	-9.75	11.86	98.5	-11.49	8.45	98.7	-11.79	8.34	98.9	-11.75	8.22
17	79.3	-30.41	18.98	80.7	-32.19	18.58	81.2	-33.69	16.89	81.2	-34.52	16.74	81.6	-34.48	16.33
18	93.9	-9.27	11.91	94.5	-10.94	10.82	95.8	-10.98	9.73	95.7	-10.63	9.85	95.7	-10.38	10.87
19	93.2	-1.50	5.75	94.4	-2.02	6.33	94.0	-2.37	5.36	94.1	-2.44	5.22	94.3	-2.44	5.64
21	94.6	-2.79	8.23	98.4	-2.89	7.93	98.4	-2.95	8.11	98.5	-2.98	8.09	98.6	-3.04	8.38
22	96.2	-9.67	5.39	96.6	-9.53	4.76	96.5	-9.44	4.71	96.2	-9.72	4.43	96.4	-9.76	4.08
23	93.4	-1.91	11.01	94.1	-2.65	8.11	94.8	-2.66	7.82	95.8	-2.94	7.30	95.2	-3.02	7.57
24	93.4	-8.51	13.28	95.2	-11.64	9.24	95.6	-11.41	8.89	95.6	-11.33	8.56	97.6	-11.54	8.71
25	95.6	-9.54	14.13	96.0	-11.15	13.25	96.8	-11.52	13.24	95.8	-11.64	13.10	95.4	-11.42	13.34
26	94.8	-9.56	12.44	95.9	-12.23	9.56	96.2	-12.21	9.04	96.7	-11.60	8.81	96.7	-11.54	8.02
27	96.2	-12.20	17.76	97.4	-12.71	16.92	98.2	-12.92	17.29	98.3	-13.02	17.00	98.2	-13.16	16.82
28	96.1	-9.53	11.80	96.2	-9.64	8.90	98.6	-9.36	8.72	98.8	-9.61	8.74	98.4	-9.42	7.48
29	93.2	-2.11	12.01	94.7	-2.23	8.56	94.9	-2.72	8.50	94.0	-2.86	8.24	94.0	-3.12	7.99
30	83.6	-30.90	1.71	85.3	-31.58	1.41	85.1	-32.42	1.55	85.1	-32.67	1.21	85.0	-31.98	1.32
31	66.8	-24.21	27.03	74.3	-25.30	24.38	74.1	-25.74	22.46	75.5	-24.56	22.19	75.0	-24.39	21.35
32	95.6	-10.68	11.39	95.8	-11.38	10.09	95.6	-11.41	9.49	96.1	-11.91	8.51	96.2	-12.15	7.25
Average	**90.3**	**-12.06**	**11.06**	**91.3**	**-13.09**	**9.94**	**91.7**	**-13.37**	**9.35**	**91.9**	**-13.50**	**8.95**	**92.1**	**-13.53**	**8.76**

As can be seen from Table 3, for the conditions of white wines unusually low values of the indicator L* (clearness) were found for some basic wines. Wines 31 (L* = 66.8), 1 (L* = 67.5), 4 (L* = 73.4) and 17 (L* = 79.3) really stand out here, but they can be joined also by wines 5 (L* = 84.0), 7 (L* = 84.7), 10 (L* = 82.0) and 30 (L* = 83.6). It is interesting that the values of L* < 80 in the first four mentioned wines were accompanied by high values of indicators a* (green direction) and b* (yellow direction). At 80 < L* < 90, high values of indicator a*, but not of indicator b*, were found. These are mostly older wines (wine 31 – 15 years, wine 1 – 15 years, wine 4 – 23 years, wine 17 – 8 years; wine 5 – 16 years, wine 7 – 10 years, wine 30 – 8 years) with relatively low content of total and, especially, free sulfur dioxide (Tables 1 and 2). The results of some earlier research show that even during a short storage period (up to 12 months) of white wines under different conditions, the L* value decreases (Hernanz *et al*., 2009; Santos *et al*., 2013). Although according to most research the L* values of white wines are over 90 units (Gómez - Míguez *et al*., 2007; Wohlfahrt *et al*., 2021; etc.), there are also reports of values of this indicator in the zone 77 to 79 units (Gamasa *et al*., 2009). Based on this, admittedly small sample, it could be concluded that older white wines, with lower sulfur dioxide content, are characterized by low values of the L* indicator and relatively high values of the a* (green direction) and b* (yellow direction) indicators. If the eight mentioned wines were to be excluded from Table 3, the newly calculated average value of L* for all remaining basic wines would be 94.7 (an increase of over 4 units), the value of a* would be -6.89 (a reduction of green by over 4 units, while the average value of b* would be 9.88 (a reduction of yellow by about 1 unit).

The data from Table 3 show that, going from sample to sample of wine, there is no clear regularity in the changes of indicators L*, a* and b* with a linear significant increase in the content of sulfur dioxide in the model wines. Thus, for example, for wine 1, a linear change of CIELAB indicators can be observed with increasing sulfur dioxide content (L*: 67,5 ↗ 68,6 ↗ 70,8 ↗ 73,1 ↗ 73,3%; a*: -13,92 ↘ -16,42 ↘ -18,16 ↘ -19,52 ↘ -20,75; b*: 25,80 ↘ 23,98 ↘ 23,02 ↘ 22,47 ↘ 21,56). However, for example, wine 5 does not have these linearly dependent changes (L*: 84,0 ↗ 84,9 ↗ 85,7 ↘ 85,3 ↗ 85,6; a: -31,09 ↘ -32,78 ↘ -33,45 ↘ 33,46 ↗ 33,37; b: 3,69 ↘ 3,36 ↘ 3,21 → 3,21 ↘ 3,19). In Table 3, from wine to wine and from CILAB parameter to parameter, different movements of the values of CIELAB parameters with a linear increase in the content of sulfur dioxide in the model wines can be found. Similar findings about the direction changes of indicators a* and b* at different experimental factors can be found in other published studies (Pérez -Magarinõ *et al*., 2003; Recamales *et al*., 2006; Carvalho *et al*., 2015). Therefore, the results of the measurements and calculations performed here do not allow conclusions about linear changes in CIELAB parameters with a linear strong increase in the content of sulfur dioxide. This, as well as the research available to the authors, do not offer sufficient explanations for the observed different movements of CIELAB indicator values in different directions, but it can be assumed that wines, each with its specific composition, react differently to increases in sulfur dioxide content, i.e., to changes in the values of CIELAB parameters with changes in the content of sulfur dioxide in wines.

Regardless to the stated different trends in changes of the CIELAB indicators' values, it was of interest to consider the average values of L*, a* and b* for all the basic wines and the average changes in their values in model wines with increased sulfur dioxide content. These values and changes in indicators L*, a* and b*, on average for all basic wines and for all experimental-model wines, are presented in Figure 1.



	Osnovno vino - Basic wine	Mod. A	Mod. B	Mod. C	Mod. D
a*	-12,03	-13,12	-13,34	-13,46	-13,49
b*	11,12	10,01	9,29	8,89	8,82
L	90,4	91,3	91,6	91,8	92,0

Figure 1. Changes in CIELAB parameter values on average for all basic and all model wines

As can be seen from Figure 1, on average for all basic and experimental-model wines, a strong increase in sulfur dioxide content led to increasing of L* values (90,4 ↗ 91,3 ↗ 91,6 ↗ 91,8 ↗ 92,0) and decreasing values of a* (-12,03 ↘ -13,12 ↘ -13,34 ↘ -13,46 ↘ -13,49) and b* (11,12 ↘ 10,01 ↘ 9,29 ↘ 8,89 ↘ 8,82). In other words, with the applied strong increases in sulfur dioxide content, the wines became lighter (in total, from the base wine to Mod. D, by 1.6 CIELAB units), greener (in total, from the base wine to Mod. D, an increase of 1.46 CIELAB units) and less yellow (in total, from the base wine to Mod. D, a decrease of 2.3 CIELAB units). It can be concluded that the first model dose of sulfur dioxide (an increase in the content found in wine by 200 mg/L) led to the most significant changes in the values of the indicators L* (about 56% of the total increase), a* (about 75% of the total decrease) and b* (about 48% of the total decrease). Other, albeit extremely high, increases in the content of sulfur dioxide in the model wines led to significantly milder changes in the values of the indicators L*, a* and b*. Chromatic indicators of the color of white wines a* and b* were characterized by some earlier research as relatively stable under changes in various experimental factors (Gil - Muñoz *et al*., 1997; Antoce *et al*., 2016), which was also recorded here at extremely high increases in content of total sulfur dioxide in wines. It should be noted, however, that research into the effect of white wine filtration on CIELAB chromatic indicators revealed small changes in the value of a*, but significant changes in the value of b* (Blesić *et al.*, 2013). Sen *et* Tokatli (2016) also recorded significant changes in the value of b* in the conditions of their research on the color of white wines.

Of particular interest for this research was the determination of the so-called total colorimetric differences between two wines (ΔE*). The indicator is calculated from the differences in the values of the indicators L*, a* and b* of the wines that are compared with each other. The ΔE* values for the comparisons made in this research are given in Table 4. It should be emphasized that the ΔE* values in Table 4 represent the values of the differences only by the rows of the table (differences between the same wine with different sulfur dioxide contents)

Table 4. Overall colorimetric difference between two wines (ΔE*)

Wine sample	ΔE*				
	Wine → Mod. A	Mod. A → Mod. B	Mod. B → Mod. C	Mod. C → Mod. D	Wine →→→ Mod. D
1	**3,28**	**2,96**	**2,73**	1,54	**9,91**
2	0,45	0,91	0,73	0,84	0,41
3	1,13	1,09	0,83	0,87	1,31
4	**5,98**	1,01	**2,34**	1,01	**6,85**
5	1,94	1,05	0,40	0,31	**2,83**
6	1,27	0,92	0,98	1,01	1,61
7	0,83	1,62	1,30	0,89	**3,39**
8	0,49	0,73	0,33	0,35	1,65
9	0,80	0,44	0,51	0,52	1,08
10	1,08	**2,43**	1,53	1,67	1,87
11	0,89	1,05	0,12	0,63	0,89
12	1,02	**4,07**	1,60	0,63	**4,77**
13	1,48	0,15	0,06	0,15	1,44
14	**3,97**	**3,86**	**2,44**	**2,94**	**7,23**
15	1,27	1,29	0,34	**2,44**	**3,68**
16	**3,24**	**3,83**	0,38	0,24	**6,26**
17	**2,30**	**2,31**	0,84	0,57	**5,37**
18	**2,08**	1,70	0,38	1,05	**2,36**
19	1,43	1,11	0,19	0,47	1,45
21	**3,81**	0,19	0,11	0,31	**4,01**
22	0,76	0,14	0,50	0,41	1,33
23	**3,07**	0,76	1,16	0,66	**4,04**
24	**5,42**	0,58	0,34	**2,02**	**6,91**
25	1,88	0,88	1,02	0,52	**2,05**
26	**4,08**	0,60	0,82	0,79	**5,20**
27	1,55	0,91	0,32	0,25	**2,41**
28	**2,90**	**2,42**	0,32	1,34	**4,90**

Wine sample	ΔE*				
	Wine → Mod. A	Mod. A → Mod. B	Mod. B → Mod. C	Mod. C → Mod. D	Wine →→→ Mod. D
29	**3,76**	0,53	0,95	0,36	**4,22**
30	1,86	0,87	0,42	0,71	1,81
31	**8,03**	1,98	1,85	0,99	**9,98**
32	1,49	0,63	1,21	1,29	**4,43**
Average	**2,37**	**1,39**	**0,87**	**0,90**	**3,73**

According to a number of research reports, ΔE* values in the range of 2.7 to 3 are considered sufficient for the human eye to clearly perceive the difference in the color of red wines (Monagas *et al.*, 2006; Martínez *et al.*, 2001; García - Marino *et al.*, 2013). Nel *et al.* (2022) state these ΔE* values as high enough for the visual perception of pink shades in white wines. On the other hand, there are also claims that in white wines a value of ΔE* of around 2.4 is not sufficient for the perception of the difference in the color of the wine by the human eye (Gómez - Míguez *et al.*, 2007a), but also claims that already at values of ΔE* of around 1 it is possible to determine the difference in the color of white wines by the human eye (Skouroumounis *et al.*, 2005). For the time being, there is a small number of studies that mention the definitive limit values of ΔE* for white wines as values at which the observer (wine evaluator) can without a doubt ascertain the difference in the colors of wines. In this direction, more detailed research on white wines, similar to those conducted on red wines, would be useful, which, after all, some researchers have called for (Gamasa *et al.*, 2009).

Relatively long ago, Spagna *et al.* (1996), without further elaborating, stated that in white wines ΔE* ≥ 2 can be considered a limit value in this respect. This threshold value, referring to Spagna *et al.* (1996), is later used by Delia *et al.* (2017) and Filipe - Ribeiro *et al.* (2021) when discussing their research results. With all the above, in this research the value ΔE* ≥ 2 was still set as a value that indicates a probably obvious overall difference in the colors of the two compared wines.

According to this, Table 4 shows that significant and probably human-perceptible changes in the color of wine occurred in 13 wines (about 42% of all wines) with the application of the first model dose of increased sulfur dioxide content in wines (increase by 200 mg/L). Here (Wine → Mod. A) the average value of ΔE* for all wines (2.37) exceeds the set critical value of 2 units as well. With further model increase of sulfur dioxide content, a smaller number of significant changes in the ΔE* value was noted. When the sulfur dioxide content increased from an additional 200 mg/L to an additional 500 mg/L, significantly high ΔE* values were observed in seven wines (about 23% of all wines). When the sulfur dioxide content increased from an additional 500 mg/l to an additional 800 mg/L, and when the content increased from an additional 500 mg/L to an additional 800 mg/L, significantly high values of ΔE* were noted in three wines each (about 10% of all wines). However, by comparing the basic wines and the final model wines (Mod. D with added 1100 mg/L sulfur dioxide), significant values of ΔE* (ΔE* ≥ 2) were found in 20 of the 31 wines analyzed (about 65%). It should be emphasized here that the color characterization of the model wine Mod. D includes accumulated changes in the color of the base wine through previous model increases in sulfur dioxide content, although these changes, as stated, in the zones of increased doses of sulfur dioxide from 500 to 1100 mg/L individually, were not often reflected in high values of ΔE*. The average value of ΔE* for all pairs of "Wine → Mod. D" comparisons are significantly high and amount to 3.73. The data from Table 4 show that seven (1, 4, 5, 7, 17, 28, 31) of the nine previously classified old white wines had significantly high ΔE* values when comparing basic wine and its Mod. D modeled wine.

It is also interesting to look at the contributions of changes in indicators L*, a* and b* to the values of $\Delta E^* \geq 2$. Data on this are not presented here, but they can be easily calculated from the values of L*, a* and b* (Table 3) and the function $\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$. The calculations showed that changes in L* had a predominant influence on the significantly high value of ΔE* ($\Delta E^* \geq 2$) when comparing "Wine → Mod. D" for five wines (14, 18, 21, 27 and 31). Changes in the value of a* had a predominant effect on high values of ΔE* also in five wines (1, 4, 5, 17 and 25), while changes in values of b* had a predominant effect on high values of ΔE* in ten wines (6, 12, 15, 16, 23, 24, 26, 28, 29 and 32). From this, it could be concluded that changes in the color of model white wines with a strong increase in sulfur dioxide content were more often the result of changes in the value of the indicator b* (decrease in the intensity of yellow color), than changes in the value of the indicator a* (shifting in the direction of green along the red-green axis) and changes in the value of the indicator L* (increased clearness of the wine).

CONCLUSIONS

Research on the influence of an extremely strong model increase in the content of sulfur dioxide (up to about 1200 mg/L) on changes in the chromatic characteristics of 31 white wines using the CIELAB method showed that with an increase in the content of sulfur dioxide, there are moderate changes in the chromatic characteristics of the wine. On average, for all basic and four model wines derived from them with high and very high contents of sulfur dioxide, an increase in the content of sulfur dioxide led to an increase in the value of the chromatic indicator L* by about 1.6 units (lighter wines), a shift in the value of the indicator a* by about 1.5 units in the direction of greener and shift in the the value of the indicator b* by about 2.3 units in the direction of less yellow. Analyzes of the value of the calculated indicator ΔE* (overall colorimetric difference between two wines) pointed out that in about 65% of the wines, the value of ΔE* (when comparing the base wine – Mod. D wine with the maximum modeled sulfur dioxide content) indicated noticeable differences in the color of the wines ($\Delta E^* \geq 2$, differences in color visible to the human eye). The biggest contribution to the value of the significantly high indicators ΔE* was given by changes in the indicator b* (shift along the yellow-blue axis in the direction of less yellow). The first model increase in the content of sulfur dioxide (200 mg/L added to the content determined in the base wine) led to the most significant changes in the values of the CIELAB indicators, so it would be useful to check possible critical thresholds of doses of sulfur dioxide up to 200 mg/L in terms of their influence on changes in chromatic properties of white wines.

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PROMJENE CIELAB HROMATSKIH SVOJSTAVA BIJELIH VINA SA MODELIRANIM VISOKIM SADRŽAJIMA SUMPOR DIOKSIDA

Sažetak

CIELAB metodom istraživan je uticaj ekstremno visokih doza sumpor dioksida (od oko 300 do oko 1200 mg/l) u eksperimnetalno-modelnim bijelim vinima pripremljenim od 31 uzorka bijelih vina iz regiona Zapadnog Balkana na promjene hromatskih svojstava vina. Spektrofotometrijskim mjerenjima i izračunavanjima su utvrđene vrijednosti CIELAB pokazatelja L* (svjetlina), a* (boja po osi crveno – zeleno), b* (boja po osi žuto – plavo) i ΔE* (ukupna kolorimetrijska razlika između dva vina). U analiziranim osnovnim vinima utvrđeni su sadržaji slobodnog i ukupnog sumpor dioksida ispod zakonski propisanih njihovih maksimalnih koncentracija u vinima koja se nalaze u tržišnom prometu. Promjene vrijednosti pokazatelja L*, a* i b* nisu pratile linearna povećanja sadržaja sumpor dioksida u eksperimentalno-modelnim vinima. Međutim, prosječno za sva vina, sa povećanjima sadržaja sumpor dioksida u navedenom rasponu dolazilo je do povećanja vrijednosti L* za oko 1,6 jedinica, do pomjeranja vrijednosti a* za oko 1,5 jedinica u pravcu zelenijeg te do pomjeranja vrijednosti b* za oko 2,3 jedinice u pravcu manje žutog. Postavljajući vrijednost $\Delta E \geq 2$ kao razliku u boji vina koja se može vizuleno (čulom vida) konstatovati, utvrđeno je da je modelno snažno povećanje sadržaja sumpor dioksida u vinima dovodilo do značajne promjene obojenosti kod oko 65% analiziranih vina. Pri ovom je najčešće preovlađujući doprinos pretpostavljeno vidljivim promjenama boje vina poticao od promjena vrijednosti parametra b*. Imajući u vidu znatne promjene obojenosti bijelih vina konstatovane u ovom istraživanju kod prvog modelnog povećanja sadržaja sumpor dioksida (za 200 mg/l) bilo bi korisno istražiti promjene boje bijelih vina pri različitim pragovima povećanja sadržaja sumpor dioksida do ovog nivoa.

Ključne riječi: *bijelo vino, sumpor dioksid, CIELAB, hromatske karakteristike vina*