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PREDICTION OF SELECTED COLOUR INDICES IN RED FRUIT WINES

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The study deals with the dependencies between indicators characterising the colored matter in cherry wines as well as three technological parameters: pH, sulfur dioxide, and alcohol. The experiment has been established in accordance with the CCRD system (Central Composite Rotatable Design) considering each of three independent variables at five different levels. Second-order polynomial equation has been fitted to each qualitative trait. It has been found that fitted models – at 0.01 level – have sufficiently described the variability of the studied wine colour indices (WC), polymeric pigment colour (PPC), anthocyanin colour (AC), colour quality (T), and chemical age of wine (CAW). Determination coefficients R^2 for those traits have been higher than 0.55, therefore the variability of each trait has been in over 55% explained by the fitted model. Fitted regression models can be used to predict studied indicators characterising the colored matter at wines.

INTRODUCTION

From the physicochemical point of view, wines are a complex system that changes during technological process. Colour, anthocyanins are responsible for, is characteristic for red wines. During wine aging, monomeric anthocyanins are polymerized. In young red wines, changes being in a balance between colored and discolored anthocyanins forms occur. New, more chemically stable compounds are formed in condensation and co-pigmentation reactions [Mazza *et al.*, 1999; Mc Dougall *et al.*, 2002; Somers & Evans, 1977]. Balance and stability of pigments depends first of all on pH value, sulfur dioxide and alcohol contents, time, temperature, presence of metal ions as well as some sugars [Bridle & Timberlake, 1997; Gómez-Plaza *et al.*, 2002].

As many authors report, the assessment of factors that affect changes of wine properties, namely compounds responsible for colour, during red fruit wine production process, is important from the point of view of their technological, biological, and organoleptic properties [Kalt *et al.*, 2000; Monagas *et al.*, 2005; Soleas *et al.*, 1997]. Wine's colour is highly correlated with taste and flavor features, and its changes overtake sensoric ones [Mc Dougall *et al.*, 2002; Monagas *et al.*, 2005].

The problem of colour of red grape wines is well described in scientific literature. The situation is inverse in the case of red fruit wines. However, it should be underlined that red fruit wines are not worse, referring to their biological properties, than the grape ones [Heinonen *et al.*, 1998].

Recently, some works upon colour of red wines using advanced statistical methods (*e.g.* multi-dimensional variance analysis or discrimination analysis) have arisen [Almela *et al.*, 1996; Gómez-Plaza *et al.*, 1999; Heredia *et al.*, 1997; Ho *et al.*, 2001; Yokotsuka *et al.*, 2000]. Their results have been the trials of statistical operating with wine aging process. However, those methods only show the process variability and allow for its continuous monitoring. When the process gets out of control, sometimes due to a variety of factors, it is difficult to tell at once, what to do to bring back the process to its balances state. In this case, it may be useful to conduct a properly planned experiment in order to optimally set the controllable factors. Preparing the experiments is also a useful tool at process design, because it allows for build process that produces goods with optimum properties, which considerably lowers the quality costs. Central Composite Rotatable Design (CCRD) is one of the methods for experiment planning. In general, it is applied when simpler system requires application of an excessive number of studied factors combinations, and measurements of examined traits are too expensive and/or labor-consuming [Montgomery, 1984].

The research was aimed at studying and describing the dependencies between sulfur dioxide and alcohol contents as well as pH value *vs*. changes of parameters characterising colored matter in cherry wines applying the CCRD method.

Achieving the adopted goals required producing red fruit wines, preparing the samples with various contents of sulfur dioxide and alcohol as well as pH values and performing the analyses including determination of indices characterising colored matter at wines. Regression analysis was performed for experimental results.

MATERIALS AND METHODS

Fruit wine was produced from cherry concentrate in accordance to rules used in wine technology [Wzorek & Pogo-

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TABLE 1. Levels of independent variables.

Independent variable	Symbol	Encoding levels				
		-1.682	-1	0	1	1.682
		Variable values				
pH	X_1	3.06	3.2	3.4	3.6	3.74
SO_2 (mg/dm³)	X_2	0	13.6	33.6	53.6	67.2
Alcohol (% vol.)	X_3	11.95	12.9	14.3	15.7	16.65

rzelski, 1998]. According to the below described experimental design, 33 wine samples (1 L each), with five different pH values, sulphur dioxide and alcohol contents were prepared. Every sample was prepared in 2 replications. Wine pH was adjusted to desired value using 1 mol/L HCl or 1 mol/L NaOH. To achieve wines with particular SO_2 contents, $K_2S_2O_5$ was applied, and to adjust particular alcohol level in the samples, 96% ethanol was used. After six-month seasoning, parameters characterising colored matter were determined in wines. Colorimetric measurements of wine color (WC), contents of dyes absorbing light at 420 nm (A_{420}), colour density (CD), colour quality (T), contents of polymeric pigment colour (PPC), and wine colour at acidic pH (WCA) were made. On the basis of the above parameters, contents of anthocyanin colour (AC), and chemical age of wine (CAW) were determined. Colorimetric measurements were made using a colorimeter Spekol 11 in accordance with the methodology used in studies upon wine color indices [Almela *et al.*, 1995; Pogorzelski & Czyżowska, 1997; Somers & Evans, 1977].

Cherry wine was characterised by the following chemical composition: pH – 3.32; alcohol – 11.95% vol.; and total acidity – 7.8 g/dm³.

Experimental design. The experiment was established according to CCRD (Central Composite Rotatable Design) taking into account each of three independent variables at 5 different levels (Table 1). All experimental designs consisted of 33 experimental points that were divided into three groups: the first one was one of traditional systems with partial replication containing 2^3 (8) points, encoding levels of which amounted to ±1 for each of three independent variables (±1, ±1, ±1); (-1,-1,-1), (-1,1,1), (1,-1,1), (1,1,-1), (-1,-1,1), (-1,1,-1), (1,-1,-1), (1,1,1); the second one consisted of 5 replications of central point (0,0,0) – their role was to estimate the experimental error; the third one was formed of 2 × 3 (6) points at the distance of $2^{3/4}$ = 1.682 from the center (±1.68, 0 ,0), (0, ±1.68, 0), (0, 0, ±1.68); from the practical point of view, these points may be considered as extreme values.

Dependencies of 8 qualitative wine's properties: A_{420} (Y_1), WC (Y_2), PPC (Y_3), AC (Y_4), CD (Y_5), T (Y_6), CAW (Y_7), and WCA (Y_8) *vs*. three independent variables: pH (X_1), SO_2 content (X_2), and alcohol content (X_3) were determined. Values of independent variables corresponding to the accepted encoding levels are listed in Table 1.

Statistical analysis. Statistical computations were performed using Statistica software. Second-order polynomial function was fitted to every qualitative trait of studied wine (Y_1 : Y_9):

$$Y_i = b_{i0} + b_{i1} * x_1 + b_{i2} * x_1^2 + b_{i3} * x_2 + b_{i4} * x_2^2 + \\ + b_{i5} * x_3 + b_{i6} * x_3^2 + b_{i7} * x_1 * x_2 + b_{i8} * x_1 * x_3 + \\ + b_{i9} * x_2 * x_3 \quad i = 1,2,...9$$

Ten regression coefficients (b_{i0}, b_{i1}, b_{i2}, b_{i3}, b_{i4}, b_{i5}, b_{i6}, b_{i7}, b_{i8}, b_{i9}) were estimated for each considered variable. Reciprocal step-wise regression was used as the fitting method. Estimations of regression coefficients, standard errors for those coefficients, beta coefficients and significance tests were calculated. Furthermore, variance analysis was performed and determination coefficients R^2 were calculated.

RESULTS AND DISCUSSION

Results from studies upon cherry wines are presented in tables and figures. Table 2 lists ranges and mean values for the analysed parameters along with standard deviations. Equations of fitted regression models, values of F-Snedecor test function, and determination coefficients R^2 are presented in Table 3. Figure 1 illustrates changes of chemical age of wine (CAW) at different combinations of three variables: pH, SO_2, and alcohol contents.

Analysis of study results revealed that the calculated estimations of regression coefficients were over twice as high as their standard errors, therefore the precision is sufficient.

TABLE 2. General descriptive statistics for tested wine's parameters.

Variable	Descriptive statistics				
	n	Mean	Minimum	Maximum	Standard deviation
A_{420}	33	2.305	2.038	3.090	0.214
WC	33	3.036	1.987	4.127	0.532
WCA	33	5.101	4.682	5.550	0.222
PPC	33	1.797	1.655	2.089	0.104
AC	33	1.281	0.255	2.260	0.548
CD	33	5.257	3.250	6.975	0.726
T	33	0.778	0.528	1.115	0.135
CAW	33	0.609	0.429	0.872	0.108

TABLE 3. Fitted regression models for tested color indices of wine, standard errors for regression coefficients (in brackets), determination coefficients R^2, and F-test values.

Dependent variable	Equation	F-test	R^2
A_{420}	$Y_1 = 4.178(0.744) - 0.1481X_1^2(0.06387) - 0.092X_2(0.040) + 0.257X_1 * X_2(0.012)$	4.020*	0.294
WC	$Y_2 = -76.451(18.967) + 48.973X_1(11.752) - 7.502X_1^2(1.643)$ $+0.011X_1X_2(0.050) - 0.003X_2 * X_3(0.001)$	13.250**	0.654
PPC	$Y_3 = 2.225(0.161) - 0.155X_1(0.047) + 0.000068X_2^2(0.00007)$	55.478**	0.787
AC	$Y_4 = -75.661(21.026) + 47.164X_1(12.393) - 7.196X_1^2(1.822)$	20.011**	0.572
CD	$Y_5 = 8.374(1.069) - 0.269X_1^2(0.0917)$	8.606*	0.217
T	$Y_6 = 23.149(4.072) - 13.400X_1(2.397) - 0.021X_2(0.009) + 2.029X_1^2(0.353)$ $-0.0001X_2^2(0.00004) - 0.0017X_3^2(0.0008) + 0.0018X_2 * X_3(0.0006)$	15.999**	0.787
CAW	$Y_7 = 21.765(3.3800 - 12.797X_1(1.992) + 1.923X_1^2(0.293)$ $+0.0001X_2X_3(0.00004)$	25.530**	0.725

X_1 – pH, X_2 - SO_2 content, X_3 – alcohol content, * - significance at 0.05 level, ** - significance at 0.01 level

It was found that fitted models at the significance level of 0.01 fairly well described the variability of indices characterising wine colour (WC), polymeric pigment colour (PPC), anthocyanin colour (AC), colour quality (T), and chemical age of wine (CAW). Determination coefficients R^2 for those traits were higher than 0.55, therefore the variability of each trait was in over 55% explained by the fitted model. Fitted regression models may be used to predict the studied wine's parameters. Models for PPC, T, and CAW are best fitted, because they explain 78.7%, 78.7%, and 72.5% of variability, respectively.

The calculated determination coefficients R^2 for A_{420} (pigments absorbing light at a wavelength of 420 nm) and for CD (colour density) were 29.4% and 21.7%, which means that only 29.4% of A_{420} variability and 21.7% of CD variability is explained by the fitted model. Therefore, the fitted models do not sufficiently describe these traits variability, thus they cannot be used for their prediction.

Regression model for WC reveals that linear (pH), then square components (pH) had the strongest influence; interactions of pH with SO_2 as well as SO_2 with alcohol had also slight impacts on that variable. Changes of WC parameter were directly proportional to pH changes and inversely proportional to a change of square component of pH. Polynomial coefficients b_1, b_2 responsible for the first and second-order dependence on pH, b_7 and b_9 determining the interaction between pH and SO_2 as well as SO_2 and alcohol, appeared to be significant. Values of regression coefficients were as follows: $b_1 = 48.973$; $b_2 = -7.502$; $b_7 = 0.011$, and $b_9 = -0.003$. Estimation of these coefficients at the above levels gives errors of 11.752 for b_1, 1.643 for b_2, 0.050 for b_7, and 0.001 for b_9, on average. The fitted equation explains 65.4% of WC variability; whereas the remaining 34.6% of that trait variability cannot be explained by the fitted model.

The level of polymeric pigment colour was affected mainly by linear pH component, and slightly by square SO_2 component. an increase of pH value resulted in PPC decrease, while square component SO_2 only slightly influenced an increase of PPC. Polynomial coefficients b_1 and b_4 appeared to be significant. Their values amounted to $b_1 = -0.155$ and $b_4 = 0.000068$. Average error of 0.047 for b_1 is made when estimating the coefficients at above levels. The fitted function describes PPC variability in 78.7%; the remaining 21.3% are not explained by the fitted model.

Pogorzelski & Czyżowska [1997] observed similar interaction between the amount of polymeric pigments and SO_2 concentration in wines accounting for it by their resistance to sulfur dioxide. Dallas & Laureano [1994] found inversely proportional dependence between PPC, pH and SO_2 content in young red Portuguese wines. Anthocyanin discoloration by SO_2 may be associated with binding the sulfite ion to a flavylic cation [Somers & Evans, 1977; Bridle & Timberlake, 1997], but the situation is more complex due to the formation of gradual SO_2 losses and formation of colored oligomers. Sulfur dioxide, as a strongly reducing agent, contributes to colour stabilization in musts and wines. However, its conservation property refers only to the non-dissociated form of sulfuric (IV) acid. Some balance between its free and bonded form is reached, which is affected by time, aldehyde concentration, temperature and environment pH [Wzorek & Pogorzelski, 1998].

Only pH value exerted a significant influence on anthocyanin colour (AC). Linear pH component had the strongest effects on that variable; increasing the pH also caused AC increase. Square pH component affected a decrease of AC. Polynomial coefficients b_1 and b_2 appeared to be significant; values of these regression coefficients amounted to: $b_1 = 47.164$ and $b_2 = -7.196$. Estimation of these coefficients at the above levels gives errors of 12.393 for b_1 and 1.822 for b_2. The fitted function describes AC variability in 57.2% and the remaining 42.8% are not explained by the fitted model.

Regression model for color quality (T) reveals that the trait varied mainly due to pH value; SO_2 and alcohol contents in wine had much weaker influence on the parameter.

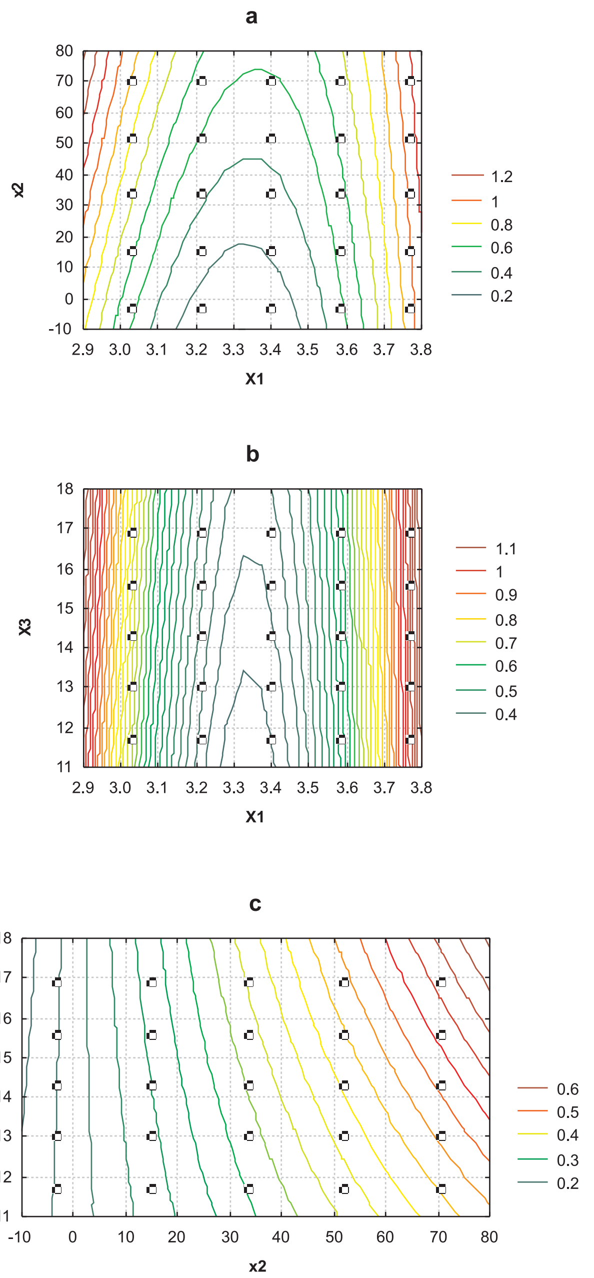

FIGURE 1. Plots of response surface for CAW of cherry wines. Surface of utility – contour lines. Method: Surface of the second degree. X_1 – wine's pH value; X_2 – SO_2 content (mg/dm^3) in wine; X_3 – alcohol content (%vol.) in wine.

Linear pH component exerted the strongest impact on T; increasing the pH caused T decrease, while square pH constituent affected an increase of T value. Also interaction of sulfur dioxide with alcohol affected the studied parameter. Polynomial coefficients b_1 and b_2, responsible for the first and second-order dependence on pH, b_3 and b_4 determining the first and second-order dependence on SO_2, as well as b_6 and b_9 related to square component of alcohol content and interaction of SO_2 with pH were also significant. Values of regression coefficients amounted to: b_1 = -13.4, b_2 = 2.029, b_3 = -0.021, b_4 = -0.0001, b_6 = -0.0017, b_9 = -0.0018. The fitted equation describes T variability in 78.7%, and the remaining 22.3% are not well explained by the fitted model.

Regression model for chemical age of wine (CAW) reveals that mainly pH of wine had an influence on the parameter; also interaction of sulfur dioxide with alcohol was observed. Linear pH constituent had the strongest influence on CAW variability. In wines with higher pH, CAW value decreased, whereas the square pH component affected a decrease of CAW. Polynomial coefficients b_1 and b_2 responsible for the first and second-order dependence on pH, as well as b_9 defining the influence of interaction of SO_2 with alcohol appeared to be statistically significant. Values of regression coefficients were as follows: b_1 = -12.797, b_2 = 1.923, and b_9 = 0.0001. Estimation of these coefficients at the above levels gives errors of 1.992 for b_1, 0.293 for b_2, and 0.000041 for b_9. The fitted equation describes CAW variability in 72.2%, and the remaining 28.8% are not explained by the fitted model. Therefore, it is good fitting and this model can be applied to predict CAW parameter.

Figure 1 presents the area of the response to independent variables and illustrates CAW variability at different sets of pH, SO_2 and alcohol levels. Figures 1a,b present the curvilinear dependence on pH and no dependence on SO_2. CAW values did not change along with SO_2 variation (contour lines from the top to bottom) – they remained at the same level and were changed only at pH changing (left and right of the center). Figure 1c presents interaction pH*SO_2.

CONCLUSIONS

Results of the performed experiments allow for finding that pH value affected the highest number of tested wine parameters, SO_2 content influenced half the studied parameters, and alcohol content did not play any significant role in shaping the wine's colour indices. Fitted models sufficiently well describe the variability of WC, PPC, AC, T, and CAW at a significance level of 0.01. Determination coefficients R^2 for these traits are greater than 0.55, thus variability of each tested property is in over 55% explained by the fitted model. Fitted regression models may be applied to predict the studied parameters of wine. Models are best fitted for PPC, T, and CAW, for they explained due to the fitted model 78.7%, 78.7%, and 72.5% of variability of the corresponding indices.

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PREDYKCJA WYBRANYCH WSKAŹNIKÓW BARWY CZERWONYCH WIN OWOCOWYCH

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W Katedrze Biologicznych Podstaw Technologii Żywności i Pasz AR w Lublinie zbadano zależności między wskaźnikami charakteryzującymi substancje barwne win wiśniowych oraz trzema parametrami technologicznymi: wartością pH, zawartością ditlenku siarki i alkoholu. Doświadczenie założono według układu CCRD (Central Composite Rotatable Design) rozpatrując każdą z trzech zmiennych niezależnych na 5 różnych poziomach. Dla każdej cechy jakościowej wina dopasowywano równanie wielomianowe drugiego stopnia. Stwierdzono, że dopasowane modele, na poziomie istotności 0,01, opisują wystarczająco dobrze zmienność badanych wskaźników barwy WC (barwa wina), PPC (barwniki polimerowe), AC (barwa antocyjanów), T (jakość barwy) oraz CAW (chemiczny wiek wina). Współczynniki determinacji R^2 dla tych cech są większe niż 0,55, zatem zmienność każdej cechy jest w ponad 55% wyjaśniana przez dopasowany model. Dopasowane modele regresji mogą być użyte do predykcji badanych wskaźników charakteryzujących substancje barwne win.