Identification of Correlations Between Chemical Substances and Sensory Characteristics of Feteasca Alba via Bravais-Pearson Coefficient

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The paper aims to highlight the direction and strength of correlations between wine chemical substances and its sensory characteristics. The study was carried out focusing on Feteasca Alba medium sweet wine which was preserved at 22.5°C for 60 days and the physicochemical and sensory analyses took place every 10 days. The experiment recorded the changes in the concentration of six chemical substances (ethyl alcohol, invert sugar tartaric acid, acetic acid, free sulphur dioxide and total sulphur dioxide) and the level of four sensory characteristics (colour, clarity, bouquet and taste). In order to ensure an accurate interpretation of data, three statistical methods were used namely Bravais-Pearson correlation coefficient, coefficient of determination and hierarchical multiple regression. The results showed strong correlations between all chemical substances (except for ethyl alcohol) and all sensory characteristics, with the highest value between invert sugar and tartaric acid relative to wine bouquet. Moreover, sensory characteristics correlate positively with invert sugar, volatile and total sulphur dioxide, and negatively with tartaric acid and acetic acid. The analysis highlights the decreased quality of Feteasca Alba since both the concentration of chemical substances and the level of sensory characteristics changed negatively. Therefore, the study does not recommend the preservation of Feteasca Alba medium sweet wine at 22.5°C.

Keywords: correlation, chemical substances, sensory characteristics, wine, Bravais-Pearson coefficient, coefficient of determination, hierarchical multiple regression

Wine has a more complex chemical composition than other alcoholic beverages, which makes it a product with an indubitable nutritional value. Most of its substances are provided by the grapes, others result from the alcoholic fermentation and some others from its aging. Besides the ethyl alcohol, the wine contains important quantities of acids, sugars, minerals, vitamins, enzymes, tannoid, colour and flavour materials and volatile substances which determine the bouquet of the wine [1]. The alcohol concentration is measured in alcoholic degrees. Ethyl alcohol is the main result of alcoholic fermentation and holds the highest proportion in wine after water. From the sensory point of view, the alcohol determines wine strength, fondness and sweetness because the alcoholic solutions in weak concentrations taste sweet, while in high concentrations they are intense. The higher its acid and alcohol content, the more balanced the sweet wine is.

Wine olfactory and taste analysis depends on the balance between the sensation of sweetness (sugars, alcohol), as a result of the acid sensation (organic and minerals acids), and the sensation of bitter (phenol components). Taking this into account, we can understand why white dry wines poor in phenols need higher acidity to establish a taste balance with alcohols, while the red wines counterbalance the lack of acidity with the presence of phenol components [2].

The volatile acidity is a key element for quality assessment and especially for wine health control. The volatile acidity is quantitatively included in the total acidity.

From a qualitative standpoint, when the wine is tasted and the presence of high volatile acidity is detected by sensory methods, its value decreases. The volatile acidity represents the result of the sum of acids in the aliphatic group, which can be found as free, but also as acid or neutral salts in the wine and can be separated from the wine through steaming. The main component of volatile acidity is the acetic acid which is accompanied in adulterated wines by large or small quantities of formic, propionic and butyric acid. The analysis of volatile components has been the focus of many empirical studies [3].

Reducing substances comprise all the sugars exhibiting ketonic and aldehydic functions and are determined by their reducing action on an alkaline solution of a copper salt [4]. There is extensive research regarding the reducing sugar content in wines that employed the spectrophotometric determination by sequential injection [5, 6], or the picrate ion-selective electrode [7]. M.C. Yebra and contributors used a continuous precipitation system for the determination of reducing sugar in different types of wine by means of atomic absorption spectrometry [8].

In wine composition, sulphur anhydride can be identified either as free or combined. Free sulphur anhydride represents the sulphur anhydride such as SO2 and mineral combination (H3SO4, HSO3 and SO32), whereas the combined sulphur anhydride is the difference between total sulphur anhydride and the free sulphur anhydride. Wine sulphur anhydride has antiseptic and antioxidant function [9].

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The Bravais-Pearson coefficient (symbolized \( r \) or \( R \)) is a dimensionless index which belongs to \([-1;1]\) interval and represents a strict linear relationship between two variables \((x, y)\) underlining the strength and direction of their correlation. The Bravais-Pearson coefficient is computed with formula (1) where \(x_i\) and \(y_i\) are the values of data sets, and \(x\) and \(y\) are their arithmetic means.

\[
R(x, y) = \frac{\sum (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum (x_i - \bar{x})^2 \sum (y_i - \bar{y})^2}}
\]

The Bravais-Pearson coefficient is used in various fields of both exact and social sciences. In medicine, the Bravais-Pearson coefficient was used in different studies regarding the optimization of electroencephalograms signals (EEG) and electrocardiograms (ECG) or in records used in the clinical diagnosis of epilepsy [10]. It was also used to compare the one-dimensional signals, multi-dimensional signals and multiple-alignments of (one-dimensional or multi-dimensional) signals [11].

Ziad S. Saad and contributors have studied a new method to improve the accuracy of MRI (Magnetic Resonance Imaging) records in neurology via Bravais-Pearson coefficient [12]. J. Gravier and contributors employed linear regression methods and Bravais-Pearson correlation matrix to control the mechanical-physical-chemical parameters of some copper surfaces used in different corrosive environments [13]. Dong-Hua Wang and contributors analyzed the CSI930 (China Securities Index 300) index futures by crossing correlation of price and trade quantity, in China [14]. Moreover, Bravais-Pearson coefficient was used in peaks separation in GC-MS or LC-MS when the identification of substances for special reasons like drugs or explosive substances is made [15].

In a recent study, two correlation matrices of sales stocks were developed in the US by two different methods, namely Bravais-Pearson correlation coefficient and the cross-correlation coefficient (DCCA coefficient). Then, the two matrices were combined with the method of random matrix theory (RMT) to achieve a statistical study about the US stocks [16].

Taking into account the extensive applicability of Bravais-Pearson coefficient, the paper employs this statistical method in the attempt to identify a series of correlations among various chemical substances in wine composition and the outcomes generated while tasting, more specifically their impact on the level of sensory characteristics.

Current literature shares different views regarding the ideal temperature of wine storage. Thus, L.R. Dopson and D.K. Hayes consider that the temperature must be between 50°F (10°C) and 65°F (18.3°C) [17], while J. Alsop argues in favour of a slightly different interval between 55°F (12.7°C) and 65°F (18.3°C) [18] and 75% relative humidity [19].

In our study, the wine was preserved at 22.5°C for two reasons. Firstly, at the beginning of the research, it was not possible to predict whether the level of sensory characteristics would change according to the variation in the concentration level of the chemical substances under study; in case the wine was preserved at the temperature and relative humidity in the allowed range limits; hence, the risk of getting uncertain results was significant.

Therefore, a higher temperature was opted for, knowing that the preservation of a food product at a temperature above the specified level will speed up the chemical reactions and generate changes in its composition [20]. Thus, a higher change in the concentration of different substances will produce variations in the level of sensory characteristics too, which will better highlight the correlations between them.

Secondly, some consumers store the wine at room temperature which ranges between 70°F (21.1°C) and 75°F (23.8°C) [21]. Given this interval, in order to ensure the objectivity of the research, the chosen temperature was 72.5°F (22.5°C) which represents the arithmetic mean of inferior and superior limit values.

Since the wine is the result of interaction of over 500 chemical components [22], its chemical composition is very complex (there are over 800 volatile substances [23]), and thus the concentration testing of all substances contained is rather difficult.

**Experimental part**

*Reagents, equipment and methods*

The reagents for reducing sugar are: alkaline copper salt solution, potassium iodide solution, 30% (m/v), sulfuric acid, 25% (m/v), starch solution, 5 g/L, sodium thiosulfate solution, 0.1 M. For alcoholic content, the suspension of calcium hydroxide, 2 M, was used.

The reagents for total acidity are: buffer solution pH 7.0, sodium hydroxide solution, NaOH, 0.1 mol/L, and bromothymol blue indicator solution, 4 g/L.

For volatile acidity, the reagents are: tartaric acid, crystalline, sodium hydroxide solution, 0.1 M, phenolphthalein solution, 1%, in neutral alcohol, 96% (m/v), hydrochloric acid (ρ = 1.18 to 1.19 g/mL) diluted 1/4 with distilled water, iodine solution, 0.005 M, potassium iodide, crystalline, starch solution, 5 g/L, saturated solution of sodium tetraborate, Na2B4O7.H2O, about 85 g/L at 20°C, acetic acid, 0.1 M, and lactic acid solution, 0.1 M.

The reagents for free and total sulphur dioxide are: phosphoric acid 85% (ρ = 1.71 g/mL), hydrogen peroxide solution, 9.1 g H2O2 (3 volumes), indicator reagent (Methyl Red, Methylene Blue, and Ethanol 50% (v/v)), and sodium hydroxide solution, 0.01 M.

The apparatus for volatile acidity is the steam distillation apparatus, which consists in: steam generator (the steam must be free of carbon dioxide), flask with steam pipe, distillation column, and condenser.

The apparatus for total acidity is made up of: water vacuum pump, vacuum flask, 500 mL, potentiometer with scale graduated in pH values, and electrodes, beakers of 12 cm in diameter.

The alcohol content testing equipment is represented by:
- the distillation apparatus, consisting of: round-bottomed 1-liter flask with ground-glass joints, rectifying column about 20 cm in height or any similar condenser, source of heat (any pyrolysis of extracted matter must be prevented by a suitable arrangement), condenser terminated by a drawn-out tube taking the distillate to the bottom of a graduated receiving flask containing several mLs of water;
- the steam distillation apparatus, consisting of: steam generator, steam pipe, rectifying column, and condenser.

The experimental part consisted in a study on Feteasca Alba medium sweet wine which was preserved at 22.5°C temperature and 75% relative humidity for 90 days.

During the 90-day period, 10 physicochemical analyses and 10 sensory analyses were performed out of which 9 physicochemical analyses and 9 sensory analyses for 22.5°C and one physicochemical analysis and one sensory analysis for 15°C (fig. 1). This situation is due to the fact that the analyses from day zero (bottling day) were carried out on wine samples preserved by the winemaker, for a few hours, at 15°C which fits in the temperature interval
mentioned above (10°C-18.3°C or 12.7°C-18.3°C) and it can not propagate errors in the present study.

Most of the times, in the physicochemical analysis of wine, the six physicochemical characteristics that are tested regardless of the type of wine are: alcohol content, reducing sugar, total acidity, volatile acidity, free sulphur dioxide and total sulphur dioxide.

The correspondence between physico-chemical characteristics and the type of chemical substance is shown in table 1.

The physico-chemical analysis of the six characteristics from table 1 was performed in accordance with the existing standardized testing methods (table 2).

In order to identify the correlation between Feteasca Alba chemical substances and its sensory characteristics, Bravais-Pearson coefficient was used for the statistical analysis. Data processing and analysis was done via IBM® SPSS® Statistics Version 21 software.

**Results and discussions**

Table 3 shows the physico-chemical characteristics level of Feteasca Alba wine preserved at 22.5°C based on the laboratory results in the 10 testing moments. Thus, the ethyl alcohol concentration remained constant, the tartaric and acetic acid concentration rose and the invert sugar, volatile and total sulphur dioxide concentration decreased.

During the 90-day storage period, it can be noticed that the most significant concentration increases and decreases, as applicable, of the substances under analysis occurred in the 90th day of preservation, and the lowest ones in the 10th day of preservation. Thus, the highest and lowest increase of tartaric acid concentration was +2.42% and +0.36%, while in the case of acetic acid the values were +16.16% and +4.65%.

As regards the three chemical substances which registered decreases in their concentration, the highest and lowest values were -2.62% and -0.58 for invert sugar, -16.77% and -4.98% for volatile sulphur dioxide, and -4.26% and -1.16% for total sulphur dioxide.

The analysis of Feteasca Alba sensory characteristics was carried out by a jury made up of three wine experts using the simple scored grading scale of up to 20 points (table 4) [24]. The tested sensory characteristics were: colour, clarity, bouquet and taste.

According to the scores in table 4, characteristics weight ranges from the highest value recorded by the wine taste...
(more than half of the total weight), followed by wine bouquet (with one third of taste weight) and wine colour and clarity respectively (with similar values which equal half of wine bouquet weight).

Table 5 presents the level of Feteasca Alba sensory characteristics tested by the experts after being preserved at 22.5°C. The score of each characteristic was obtained by calculating the simple arithmetic mean of the experts' scores after assigning integer numbers according to the interval specified in column 3 of table 4 above.

Compared to the wine chemical substances which registered increases and decreases at a continuous rate, all sensory characteristics kept decreasing and, at times, kept constant.

The most important decreases were in the case of wine colour by -40% (in the 90th day of preservation), wine clarity by -23.08% (in the 70th day), wine bouquet by -20% (in the 90th day) and wine taste by -4% (in the 70th day).

In contrast, the lowest decreases were recorded by wine colour and clarity by -18.75% (in the 50th day of preservation), wine bouquet by -8.33% (in the 20th day) and wine taste by -2.65% (in the 10th day).

Consequently, processing the data in tables 3 and 5 resulted into the matrix in table 6 which consists in independent variables (chemical substances on the rows) and dependent variables (sensory characteristics in the columns) based on.

Each cell of table 6 contains the following information regarding the combination between one chemical substance and one sensory characteristic:
- Bravais-Pearson coefficient value ($R$);
- significance level - Sig. (2-tailed);
- number of entries ($N$).

Irrespective of the algebraic sign of Bravais-Pearson coefficient in table 6 (which highlights only the direction of the correlation), it can be noticed that invert sugar highly

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<table>
<thead>
<tr>
<th>No.</th>
<th>Sensory characteristic</th>
<th>Score interval of each characteristic (points)</th>
<th>Characteristic weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Colour</td>
<td>0-2</td>
<td>10</td>
</tr>
<tr>
<td>2.</td>
<td>Clarity</td>
<td>0-2</td>
<td>10</td>
</tr>
<tr>
<td>3.</td>
<td>Bouquet</td>
<td>0-4</td>
<td>20</td>
</tr>
<tr>
<td>4.</td>
<td>Taste</td>
<td>0-12</td>
<td>60</td>
</tr>
<tr>
<td>5.</td>
<td>TOTAL</td>
<td>20</td>
<td>100</td>
</tr>
</tbody>
</table>

**Table 4**

SIMPLE SCORED GRADING SCALE OF 20 POINTS

<table>
<thead>
<tr>
<th>No.</th>
<th>Preservation period (days)</th>
<th>Sensory characteristic</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Colour (points)</td>
</tr>
<tr>
<td>1.</td>
<td>0</td>
<td>2.0</td>
</tr>
<tr>
<td>2.</td>
<td>10</td>
<td>2.0</td>
</tr>
<tr>
<td>3.</td>
<td>20</td>
<td>1.6</td>
</tr>
<tr>
<td>4.</td>
<td>30</td>
<td>1.6</td>
</tr>
<tr>
<td>5.</td>
<td>40</td>
<td>1.6</td>
</tr>
<tr>
<td>6.</td>
<td>50</td>
<td>1.3</td>
</tr>
<tr>
<td>7.</td>
<td>60</td>
<td>1.3</td>
</tr>
<tr>
<td>8.</td>
<td>70</td>
<td>1.0</td>
</tr>
<tr>
<td>9.</td>
<td>80</td>
<td>1.0</td>
</tr>
<tr>
<td>10.</td>
<td>90</td>
<td>0.6</td>
</tr>
</tbody>
</table>

**Table 5**

SENSORY CHARACTERISTICS LEVEL OF FETEASCA ALBA PRESERVED AT 22.5°C

**Table 6**

BRAVAIS-PEARSON COEFFICIENT VALUES ($R$) FOR FETEASCA ALBA PRESERVED AT 22.5°C

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* Correlation is significant at the 0.01 level (2-tailed).

a Cannot be computed because at least one of the variables is constant.
correlates with wine bouquet (.994), its relation with wine clarity (.935) proves lower.

In a similar way, tartaric and acetic acid highly correlate with wine bouquet (.994 and .993 respectively), while their relation with wine clarity registers lower coefficient values (.926 and .909 respectively).

A different situation is recorded by volatile sulphur dioxide whose highest coefficient value relates to wine taste (.990) and the lowest to wine clarity (.958).

In the case of total sulphur dioxide, the highest coefficient value is recorded in relation to wine bouquet (.993), and the lowest to wine clarity (.944).

As it was mentioned before, the values of Bravais-Pearson coefficient lie between \([-1;1]\). In order to explain the strength and direction of the correlation, there are five sub-intervals in which coefficient values can be included (table 7) [25].

In light of the computed values of Bravais-Pearson coefficient (table 6) and the corresponding intervals (table 7), one can notice the strong correlation between chemical substances (invert sugar, tartaric acid, acetic acid, volatile and total sulphur dioxide), on the one hand, and wine sensory characteristics (colour, clarity, bouquet and taste), on the other hand, since the coefficients level belongs to \([0.80;0.99]\) and \([-0.80;-0.99]\), as applicable.

All Bravais-Pearson coefficient values in table 6 have a significance level lower than .05 (\(p=.000\) is reported as \(p<.001\)) which means that the probability to fail is less than .1%.

The only chemical substance that does not influence the four sensory characteristics is ethyl alcohol because its concentration remained constant during the entire preservation period which is highlighted by the absence of Bravais-Pearson coefficient values and its impossible computation due to at least one constant variable (see comment “a” right below table 6).

The direction of the correlation between chemical substances and sensory characteristics, in the case of Feteasca Alba preserved at 22.5°C correlates with wine bouquet (.994), its relation with wine clarity (.935) proves lower.

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The direction of the correlation between chemical substances and sensory characteristics, in the case of Feteasca Alba preserved at 22.5°C is shown in figure 2. Thus, the tartaric acid and acetic acid are in negative correlation with sensory characteristics, whereas the invert sugar, volatile sulphur dioxide, total sulphur dioxide are in positive correlation with sensory characteristics.

In most cases, in order to provide a more accurate interpretation of Bravais-Pearson coefficient values, the coefficient of determination is calculated by squaring the correlation coefficient. The coefficient of determination underlines the variation of the dependent variable which can be explained by the independent variable variation and it can range from 0 (the independent variable accounts for 0% of the variation of dependent variable) to 1.00 (the independent variable accounts for 100% of the dependent variable variation) [26, 27].

Figure 3 presents the coefficient of determination for Feteasca Alba preserved at 22.5°C. Thus, it can be noticed that the variation of wine colour is mostly influenced by the variation of invert sugar (94.87%) and least by acetic acid (92.35%). As regards clarity, its variation is mostly influenced by volatile sulphur dioxide (91.78%) and least by acetic acid (82.63%).

The different status of wine bouquet is due to the variations of invert sugar and tartaric acid having the highest impact (98.8%) and volatile sulphur dioxide the lowest (96.63%). The wine taste depends mostly on the volatile sulphur dioxide variation (98.01%) and least on acetic acid (93.51%).

The coefficient of determination based on the correlation coefficient (fig. 3) allowed only the identification of the influence of only one chemical substance variation in Feteasca Alba over a single sensory characteristic. Nevertheless, by hierarchical multiple regression, the computed coefficients of determinations are able to capture the cumulative influences of each new chemical substance successively introduced in the analysis (table 8).

The coefficient of determination values in table 8 differ from those in figure 3 except for the values of invert sugar relative to wine colour, clarity, bouquet and taste, which reflect the association of a single chemical substance with a single sensory characteristic.
Conclusions

Wine colour variation is explained by invert sugar influence in a high percentage of 94.8% and it can rise by 1.5% due to additional interference of tartaric or acetic acid, by 0.8% in the case of volatile sulphur dioxide and only by 0.1% once total sulphur dioxide is introduced.

As regards wine clarity, its variation of 87.4% is explained by the invert sugar variation, successively increasing with each new chemical substance which is integrated in the analysis, as follows: 4.9% once with tartaric acid, 1.5% with acetic acid, 0.5% with volatile sulphur dioxide and 0.9% with total sulphur dioxide.

Wine bouquet variation of 98.8% is explained by the variation of invert sugar. This percentage rises by 0.1% once the tartaric acid is introduced, by 0.1% in cases like acetic acid or volatile sulphur dioxide and by 0.6% when adding total sulphur dioxide.

As for wine taste, its variation of 96.5% is also due to the variation of invert sugar, increasing by 2.4% when introducing the tartaric or acetic acid and by 0.1% in the case of volatile or total sulphur dioxide.

Overall, it can be stated that the quality level of Feteasca Alba medium sweet wine has decreased at the preservation temperature under study, and this can be due to the decline in the concentrations of invert sugar, volatile and total sulphur dioxide, as only the concentrations of tartaric and acetic acid have risen. On the other hand, the level of sensory characteristics recorded mainly reductions with insignificant stagnations depending on the testing moment. To conclude, the study proves that the preservation temperature under study, and this can be due to additional interference of tartaric or acetic acid, by 0.8% in the case of volatile sulphur dioxide and only by 0.1% once total sulphur dioxide is introduced.

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