THE RELATIVE INFLUENCE SCORE METHODS, THE DETERMINATION OF THE ALCOHOLIC STRENGTH OF RECAŞ WINE. CORRELATION INDEX

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Summary: Direct, indirect, simple, elaborate or rapid methods for determining the alcoholic strength of wines were analyzed in this study were established correlation between values obtained with: using physical methods of direct and indirect variant producing results, the technique of obtaining sample for analysis in indirect methods, principle of operation of the apparatus used to determine correlations between direct and variant principle of the direct method and the indirect infiltration stage of sample preparation that is specific for alcoholic extract. Important parameter value alcohol concentration generally well correlated: $R^2 = 0.9409$, white wine and $R^2 = 0.9146$ for red wine for all methods used in this study. For critical points, such as distillation separation of the alcohol as a method of correlation of $R^2 = 0.9957$ was white wine and red wines $R^2 = 0.9146$. In general it can be said that the law of the vineyard and wine label must include the value of this flag, so the data obtained can use any value obtained by any of the methods used in this study and developed equations can be used to predict concentration values using homologous method.

Keywords: wine alcohol, ethanol, densimetric analysis, procedure sample distillations, pretratament procedures

Introduction

Recaş, Banat area ranks fifth on the wine market in Romania(Iancu, ML., 2013). Currently operating Recaş about a thousand acres of vineyards located in Recaş. Recas wines are exported in aprox. 25 countries including the UK, U.S., Germany, Japan, Canada, Russia, Netherlands, Czech Republic, Slovakia, Sweden, Estonia, Australia and others(www. recaswine.ro, 2014). Alcohol content of wine is an important indicator for production and quality control (Anthony L. Robinson, et al, 2014). It defines wine an a undistilled alcoholic beverage is obtained solely from the fruit of the vine grapes, fermentation(Tiţa, O., 2001). The natural alcoholic strength is the total alcoholic strength of the product before any enrichment invigorator (concentrated must mistel, grape sugar, sugar food, refined alcohol distilled from wine, etc.). Alcoholic strength and content of sugars can be used in calculating the total alcoholic strength (Tiţa O., 2001). Alcoholic degree(strength) natural wines varies between

8 ÷ 16 % vol., most commonly between 8 to 14% vol., and the label must contain the value of this indicator(Colins, TS, 1997, Law Vine and Wine, 2002). Demanding requirements of consumers in recent years and the willingness of domestic producers to export as much as the European Union countries, as Romania in 2007, makes the issues of quality, safety and authenticity of alcoholic beverages to increasingly preoccupy the Romanian producers. New methods of checking the products are implemented every year, authorities using these methods to identify potential counterfeiters in the production of alcoholic beverages. Analyses such as capillary electrophoresis(Colins, TS, et al, 1997)

spectrophotometric method(dichromate oxidation spectrophotometry) (Caputi, A., et al, 1968 AOAC method, 1990, Anonymous, 1992), NMR analysis applied to verify the authenticity of wines, gas chromatographic method for checking the quality and safety of alcohol(Oliviera, MJ, 2006, Arcari, GS, et al, 2013), capillary gas chromatography (Wang, ML., and others, 2003) enzymatic methods (McCloskey, I.,P., et al, 1974, Mason, M., 1983, Jones, AW, 1995) used until a few years ago just for research purposes, without being applied by manufacturers and authorities helps to check the quality and safety of wines and other drinks (Rusu, E., 2011). The ethanol can be used in the analysis of biosensors(Jones, AW., 1995), potentiometry(Kokovkin, V. V., et al, 1995), high performance liquid chromatography, HPLC(Kupinica, SA , et al , 1984, Martin, F., et al, 1986). It is also used to dispense alcohol chemical method(Anonymous, 1992 AOAC, 1990, Caputi, A., 1969). In practice the determination of alcoholic strength not distinguish between alcohol and his counterparts there in very small quantities in wine. The entire assembly is measured as the alcohol volatile alcohol. Expression alcohol concentration(to two decimal places) is in percent by volume (% vol.) at 20 °C(late C., 2007). These assay methods are direct and indirect methods(SR, 2010). Direct methods are ebulliometer method (Iancu, ML. 2013) and near infrared spectroscopy(Van den Berg, F., et al., 1997). Indirect methods are those separated from the beverage alcohol extract by simple distillation or steam distillation entrainment. Distillate obtained is analyzed using methods based on physical principles and all the fractions is determined by the alcohol concentration in the sample and the result is expressed as % v alcohol/v. In this study we aimed to achieve alcohol concentration value expressed in % v/v, using direct and indirect methods of analysis, standardized or used only in research. Was aimed to correlate these results. This was clear and the objective of this research. Processors wine complained difference between the classical determinations, standardized and modern apparatus have appeared on the market recently and can not be given in the report. Were analyzed for the Romanian wines of Recaş, white and red. Modern techniques using modern devices involve the use of small samples, ease of use is incomparably more effective, working time is short and the sample is automatically thermostated. So why not use modern methods result in official bulletins of analysis?

Materials and Methods

Was used for determinations come from production of 2012, which comes from the vineyard Recaş, white and red wine whose characteristics were determined. For the distillation of the sample using simple distillation unit consisting of 500 ml distillation flask, and the evaporator dephlegmator. Heating was done with a nest of heating with adjustable temperature. Drive steam distillation was performed with the *ALCO–TEST* which is a semi–automatic tester for determination degree alcohol, volatile acidity and sorbic acid. It is a distillation unit, electric steam generator. Analysis was done using the hydrometer distillate, alcoholmeter(EEC Reg 2676/90), pycnometer, portable electronic densitimeter *DMA–35*(Ghidossi, R., et al, 2012), Alkoltest site is a water– alcohol binary mixtures analyzer. Alkalisation of the wine before the distillation is carried out using sodium hydroxide solution 2N concentration. Control was made alkaline outside litmus test solution on a plate wells(Tiţa O., 2001). Using battery ebulliometer determined the boiling point of water and wine, and using specific calculation methods to determine the alcoholic strength of the wine. In order to determine the alcoholic strength directly used

Alcolyzer Anton Paar wine, by means of near infrared spectroscopy(NIR) is based on the interaction between the radiant energy for analysis and measurement of the light absorption intensity.

Table 1. Table of abbreviations used in the interpretation of results

Abbreviation (code)	**Deciphering the code**
AR–SDE	Distillate obtained by steam distillation entrainment and analyzer with areometer
AR–DS	Distillate obtained by simple distillation and analyzed by the hydrometer(areometer)
EB	Ebulliometer
ACY	Alcolyzer wine
DE–SD	Distillate obtained by simple distillation and analyzed by Densitimeter portable electronic
DE–SDE	Steam distillation entrainment and and analyzed by Densitimeter portable electronic
AK–SDE	Steam distillation entrainment and analyzed by Alkotest
PC–SD	Distillate obtained by simple distillation and analyzed by Pycnometer
PC–SDE	Distillate obtained by steam distillation entrainment and analyzed by Pycnometer
AK–SD	Distillate obtained by simple distillation and analyzed with Alkotest
AL–SD	Distillate obtained by simple distillation and analyzed with Alcoholometer
AL–SDE	Distillate obtained by steam distillation entrainment and alnalzyed with Alcoholometer

The distillate obtained is analyzed using methods that are based on physical principles. For determining the relative density is used areometry, pycnometric, portable electronic densitimeter. On the basis of the values obtained determine the alcoholic strength wine tables analyzed.

Results and Discussion

To analyze the alcohol concentration were used samples of white wine and red wine have been identified and other quality indicators that can be used in the classification of wines. Thus white wine has a value of total extract 26,87 g/l and red wine 35,55 g/l (table no.2). It falls into the category of semi–dry wines if the sugar content is low and after taste characteristics.

Table 2. Physico chemical wines Recaş

No. crt.	**Indicators of quality**		**White wine**	**Red wine**
1	Alcohol concentration, [% (m/m)]	ALCOLYZER– wine	9,7	9,91
2	Density wine, [g/cm^3]	DMA–35	0,9925	0,9955
3	The relative density of the extract	ALCOLYZER– wine	1,01036	1,01317
4	Extract total, [g/l]	ALCOLYZER– wine	26,87	35,55
5	The relative density of the wine	ALCOLYZER– wine	0,99429	0,99729

Using portable electronic densitimeter determined density and relative density Wine(table no. 2) and found that this indicator of quality is influenced by the assortment of wine and its dry matter content. Wine density value thus determined is used as input, independent calculation program other quality indicators determined by the analyzer "Alcolyzer wine".

In light of its purpose, namely to establish the correlation between the methods for determining the alcoholic strength settled screeneng addiction. Thus in Figure 1 were represented alcoholic concentration values obtained by different methods(Table 1). Methods using physical principles underlying the operation of various devices used. It is noted that the figures obtained are in the same range of values of the alcohol concentration that are otherwise comparable both in white wine and red wine. The regression equation obtained from the linear mapping point cloud(1) and the correlation coefficient R^2 = 0.9146 shows a good combination of alcohol concentration values expressed in %(v/v) obtained by different methods, after the complete physical principles different, for red wine.

$$Y_{\text{red wine}} = -0{,}2436\ x + 14{,}092 \quad (1)$$

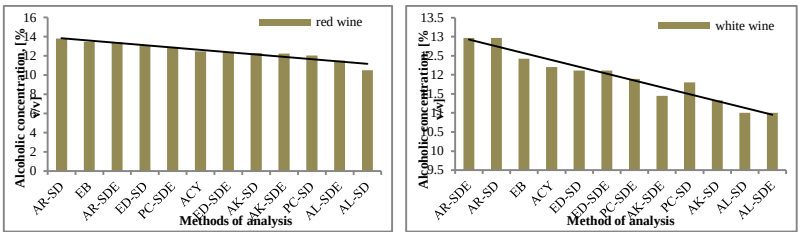

Fig. 1. Correlation alcohol concentration values expressed in % (v/v), red and white wine, by using the direct and indirect physical methods known (abbreviations, table no.1)

Correlation of white wine sample (Fig. 1.) is R^2 = 0.9409 is very good. Linear regression equation(2). It is noted, however, that the alcoholic strength values are much different, each in the red versus white wine.

$$Y_{\text{white wine}} = -0{,}1791\ x + 13{,}102 \quad (2)$$

Regression functions are polynomials of degree, the size of x is input coefficient has a negative value as in equation(1) and the equation(2). This shows that the numerical values for alcoholic were represented in descending order. The regression results are visualized graphically by plotting the point cloud and the schedule of the regression (1) and (2) the independent variable, x, with a sufficiently small step and calculated the dependent variable, y. So for any $x \in [10.5;13.8]$ red wine and

$x \in [11;12,97]$ white wine, the range of values determined for alcoholic wine, intermediate values, we get the "cloud" values for the dependent variable y. As it can be seen from the above results it is not a perfect correlation, further graphics were made and to determine the correlation between the critical points of the methods used. Was established as critical points: direct version and indirectly by producing results, the technique of obtaining the sample for analysis in the indirect methods, the principle of operation of the apparatus used to determine correlations between direct and variant

principle of the direct method and the indirect infiltration stage of obtaining the sample analysis specific for alcoholic extract. It has been shown in Fig. 2 the correlation between alcohol concentration values expressed in % v/v, obtained by direct methods of analysis, namely the ebulliometer *Salleron Dujardin* method(standard method) and the method of analysis, the spectrum of radiation in the near infrared range(NIR). Correlation values for white wine is made by a 2nd order regression equation and correlation index is R^2 = 0.7334 . In this equation it is seen that the coefficient size of the input x is high which means that the regression polynomial approximation is well chosen. The values obtained for alcoholic white wine by direct methods are within the range [12.2;12,5], represented by pairs of points. For red wine, but the correlation is not so good R^2 = 0.3993. It seems that due to higher alcohol concentration of red wine producing these results.

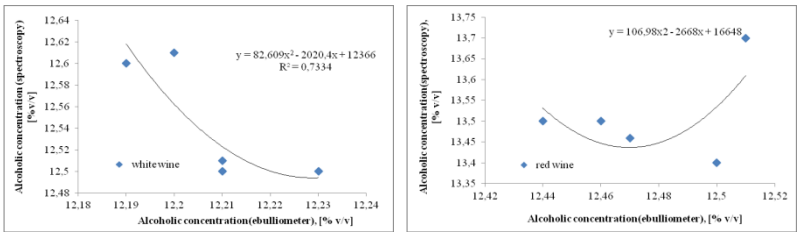

Fig. 2. Correlation alcohol concentration values expressed in % v/v, for red and white wine by using the direct methods (5 value–ebulliometer and spectroscopy) to determine

The higher alcohol may influence the boiling point of the mixture to be analyzed and the absorbance read value as input to the spectroscope sofware. The two direct methods using different sample quantities. Thus, the EB is used thermostated

50 ml sample at the time of measurement compared to the method of ACY to 5 ml and are used when determining the sample is thermostated to 20°C. So not recommended comparing the alcoholic strength of the wine country, using these methods of determination. In fig. 3 are the correlations between the results obtained by the methods of obtaining a sample for analysis. The only common point is the separation technique, namely alcohol distillation. The critical point is that while simple distillation collected volume measuring ¾ of the original volume of wine made alkaline to steam distillation entrainment literature but does not specify an exact amount at least equal to the volume of wine sample analyzed. After several determinations concluded that it is better to collect the same amount of distillate equal to that of wine. To assess correlations and demonstrate that the volume is well chosen were issued regression equations that can be predictive. It is observed that the correlation is very close to 1 for the sample of white wine. In red wine sample has a higher alcohol concentration correlation is weaker (Fig. 3).

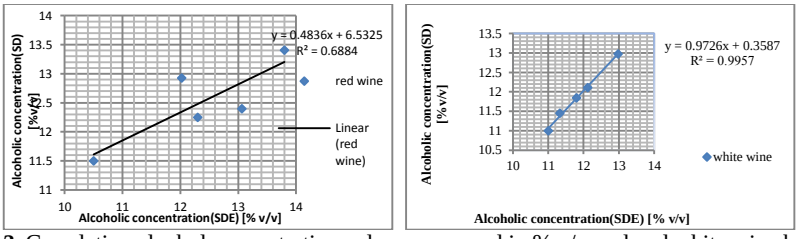

Fig. 3. Correlation alcohol concentration values expressed in % v/v, red and white wine by the analysis of samples obtained by simple distillation(SD) and steam distillation entrainment(SDE) and use physical methods of analysis of the distillat

Size alcohol concentration is the same range of values which means that the method of obtaining the sample is well established to drive variant steam distillation. For example, if the sample of white wine distillate is analyzed using methods that are based on the gravitational attraction, which are considered to be highly subjective to obtain the same value at 11 % v/v (areometer) and 12.97 % v/v (areometer specialized – alcoolmeter) concentration. Pycnometer method which is based on weighing a precisely measured volume provides comparative results: 11.8 % v/v, respectively 11.85 % v/v. Using portable elecronic densitimeter which operates by " U –tube " values are identical 12.11 % v/v. Alkotest which is based on ultrasonic technology, read values comparabl for the two types of samples 11.33 % v/v, simple distillation, and 11.45 % v/v in the sample obtained by steam entrainment distillation. In red wine values are also comparable but the differences are slightly larger in the red wine because higher alcohol content. For example, the pycnometric method to obtain 12.02 % v/v (SD) and 12.93 % v/v(SDE) densitimeter portable electronic 13.06 % v/v, respectively 12.4 % v/v. It can be said that the differences in values are given that amount of alcohol measured is directly proportional to the principle physical measurement used. If using direct methods of analysis of the alcoholic strength of wine quality indicator values can be influenced by the presence of other substances such as the sugars, acids, tannins, polyphenols, higher alcohols and other substances. When analyzing binary water–alcohol mixture values for alcoholic strength may be different from those obtained from direct methods. In fig. 4 are plotted the addicted both white wine and red wine. Physical methods for the analysis of the distillate are the same date. Although white wine correlation methods of sample preparation was good, fig. 3 , in fig. 4, for the white wine there is a very poor correlation. Regression equations are 2nd order polynomial coefficient values lower. This means they cannot be recommended for use in predicting values. Red wine is very good correlation coefficient for both simple distillation and steam distillation to drive. Due to the higher content of alcohol in red wine data errors influence of other substances in wine was depreciated.

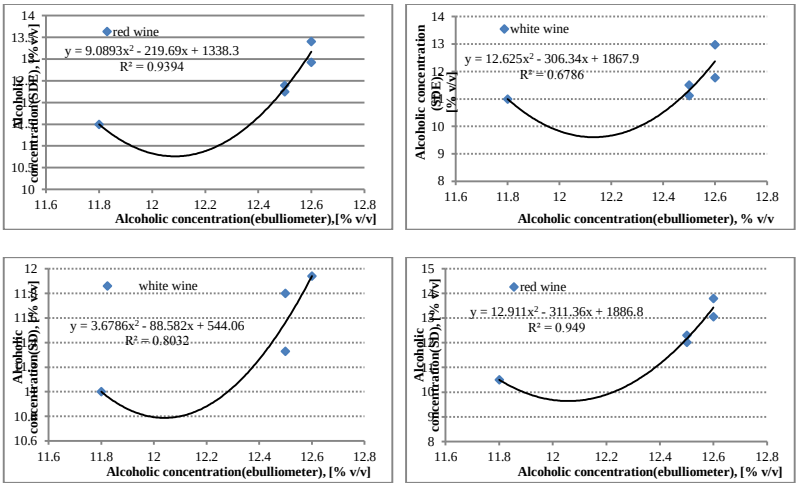

Fig. 4. Correlation alcohol concentration values expressed in % v/v, the red and white wine by the analysis of samples obtained by simple distillation and steam distillation entrainment and method ebulliometer

As a research perspective aims studies comparing these values with the values obtained will be obtained in quantitative analytical determinations, chemical dosing alcohol and analysis by gas chromatography, only alcohol that is considered to be the method most accuracy in determining the alcohol content of wine.

Conclusions

As a general conclusion it can be said that in general the factors influencing the quality indicator values determined are: assortment of wine, the principle underlying the determinations, the amount of sample taken in the analysis of data in developing permutation graphs. Direct and indirect methods used to determine the alcoholic strength of the wine can be used by removing and because good correlations debited equations can be used in prediction values, with few exceptions such as the correlation between direct methods for wines with a higher concentration of 12% v/v. It can analyze binary mixtures of water–alcohol obtained by simple distillation and steam distillation drive the wine, and the results are comparable. Variant correlations between direct and indirect method principle infiltration in stage of sample preparation that is specific for alcoholic extract can conclude that if the wine has an alcohol concentration of less than 12 % v/v due to substances up extract wine results do not correlate than 80%, and the average proportion of the strong wines 93.5 %. According to the law of the vineyard and wine label must include the value of this flag, so the data obtained it is recommended to use any value obtained by any of the methods used in this study.

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