THE ANALYSE OF PHYSICO-CHEMICAL PARAMETERS MEANS TO APPRECIATE THE TYPICITY OF SOME RED WINES

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Abstract. *Depending on soil, weather characteritics (temperature and precipitations) and varieties, every wine has its own fingerprint. This fingerprint helps to establish the authenticity of wines. At the same time, chemical analyses of wine quality are important in establishing their composition parameters. We intend to set down some characteristics for several varieties of Romanian wines produced in the Valea Calugareasca region. In this paper we present our results for two wines: Merlot (2006) and Feteasca Neagra (2007). To reach this goal, we used different analytical methods: optical methods (refractometry, polarimetry and colourimetry), spectrometer methods (UV-VIS), electrochemical methods (potentiometry). The preliminary examination of samples includes colour analysis and microbiological stability. Mention should be made that the studied wines are stabilized and did not contain viable yeast cells. Using the CIE – Lab – 76 method we objectively determined the colour of wine: Fetească Neagră – 2007 is red brick, and Merlot – 2006 is intense red. Then, for each wine we determined: minimum alcohol content (alcoholmeter titer), relative density, total acidity, contents of methanol, glycerol, acetaldehyde, SO_2 and anthocyanins. The characteristics obtained from chemical analysis are normal for these wines, but do not present the typicity of the Valea Calugareasca area. Finally, using the data from all the studied wines, we intend to create an analytical database for wines produced in this region.*

Keywords: *CIE – Lab – 76, fingerprint, analytical database, authenticity*

Introduction

Wine analysis is a laborious and expensive work. As the analytical results should be useful, they must express the real physico-chemical parameters of wine composition, based on the establishing of wine quality. The typicity and authenticity of wine are basic attributes that generate the wine quality. The criteria for checking the authenticity of red wines are: the anthocyanins' spectrum, the fingerprint of amino acids, the wine's alcohol and water isotopic composition[6]. The features of variety due to the vineyard and production technology give the wine typicity.

In the preliminary analysis of the studied samples, we took into account the colour of wines (objectively determined, using colour space) and their microbiological stability.

Yeasts are microorganisms with a considerable influence on quality and value of wine[1,2]. Yeasts guide the alcoholic fermentation and contribute to achievement of the typicality of wine savour and fragrance. In the winemaking process, yeasts may lead to the depreciation of wine quality and consequently the decrease of wine value, after alcoholic fermentation. The development conditions determine the useful or harmful nature of wine microorganisms and this is the main problem for the oenologist[3].

The wine microbiota could contribute to wine quality with the final products of

alcoholic fermentation. The optical method is one of the favorite techniques for the inspection of wine quality, because it is fast, simple and versatile[4].

To establish the quality of wine, the chemical analysis can provide information about the natural character and the grapes origin only, without the presence of any fraud or impurity.

In this paper we studied the characteristics of different red wines from Valea Calugareasca area, using different analytical methods: optical, spectrometric and electrochemical ones. In fact, our goal was to set down the *fingerprint* for each of these wines and finally, using all our data about another Romanian wines, to get a database and establish their authenticity and eliminate fraud.

Materials and methods

Our studies were made on many sorts of wines, from different areas, but in this paper we present just only two of them: Merlot (2006) and Feteasca Neagra (2007) – Valea Calugareasca area, important vine area for red wine production.

We started the wine analysis with an important stage: preliminary examination of samples. This includes colour analysis and microbiological stability. Usually, shade and intensity of wine colour are calculated by optical methods[5]. But CIE established that colour could be exactly defined by chromatically parameters: lightness, chromaticity and purity. Thus, we used the spectrophotometrical method in tri-stimulus coordinates (CIE – Lab – 76) for colour analysis as parameter of wine quality. The absorption spectra were measured on a Perkin Elmer Lambda 25 UV-VIS spectrophotometer, with double fascicle. Basing on transmittance values, we determined the colour coordinates (x, y) for every sort of red wine.

The microbiological control was achieved by cultivation of wine decimal dilutions on solid medium YPG (yeast extract - peptone glucose) at 28ºC for 24 hours. This step was part of indirect technique for the determination of number of viable cells (CFU/ml), to assess the yeasts' microbiota of the investigated wines.

Then, a very large set of chemical analyses were performed. For each wine we determined: minimum alcohol content (alcoholmeter titer), relative density, total acidity, contents of methanol, glycerol, acetaldehyde, SO_2 and anthocyanins.

The alcoholmeter titer, one of the most important parameters of wine quality, was determined by indirect method, (pycnometer method), after prior separation of alcohol from wine by distillation.

Acidity provides physico-chemical stability of wine, gives colour, brightness and freshness of taste. To characterize acidity of wine the following types of acidity are taken into consideration: total acidity, volatile acidity, fixed acidity and ionic/ real acidity of wine. The determination of total acidity was made by titration with bromothymol blue. The method consists of wine sample titration (acid neutralization) with a solution of sodium hydroxide in the presence of bromothymol blue, after prior removal of carbon dioxide. The evaluation of total acidity in mechiv./liter is the most appropriate, because it is an unitary mode to quantify acids and substances with acid reaction in wine. To determine the fraction of volatile acidity, it is separated from wine by steam stripping of volatile acids in wine. Once separated from wine, it is determined from the distillate obtained by titration with an alkaline solution of sodium hydroxide in the presence of phenolphthalein as indicator. Sulfur dioxide and sorbic acid, resulting from distillate and not being part of the volatile acidity of wine, are determined separately and they are subtracted from volatile acidity.

The dosage of metatartric acid from wine was made by the precipitation with cadmium acetate.
Usually, citric acid in wine is determined by spectrophotometer method using acetic anhydride. The method is based on the reaction of citric acid in wine by acetic anhydride in basic medium; a compound with a maximum absorbance at 363 nm is formed.
The total remaining unfermented sugars in wine were evaluated by refractometric method, by measuring the percentage of soluble solids or refractive index, after prior removal of alcohol and volatile compounds from wine (which changes the refractive index value).
Sulphur dioxide is the only antiseptic allowed in wine conservation. The determination of free SO_2, combined SO_2 and total SO_2 is rapidly made by using iodometric oxidation.
The anthocyanins are visible phenolic compounds (pigments), which are getting accumulated in grapes and give red colour to wine. They represent 38 % of the total phenolic compounds present in wine.
The quantitative determination of anthocyanins is made by visible spectrophotometry and is based on the change of anthocyanins colour depending on pH. We measured the absorbance variation of anthocyanins colour at two pH values, 0.6 and 3.5, and compared with distilled water. The measurements were made at 520 nm, the absorbance of the samples being proportional to the anthocyanins content.
The methanol determination is made after its separation from wine (by distillation), by spectrophotometric dosage. The methanol from the wine distillate is oxidized to formaldehyde with potassium permanganate, acidified with phosphoric acid. The aldehyde amount is proportional to the methanol content in wine. Then, the formaldehyde is dosed with chromotropyc acid (colour reaction), colour intensity being measured by spectrophotometer at 575 nm.
The determination of polyhydric alcohols in wine was made using volumetric method, by oxidation with periodic acid. The method involves the prior defecation of wine, followed by separation of glycerol and butilenglycol by extraction with different solvents. The separated glycerol is cold oxidized by periodate potassium in excess, to formaldehyde and formic acid. Then, the excess periodic acid is titrated with sodium thiosulfate.
Acetaldehyde is the compound that represented 90% of the total of wine aldehydes. Its determination was made by volumetric method, acetaldehyde being separated from wine (by distillation) and fixed in a combination aldehydo-sulfur.

Results and discussion

The preliminary analysis shows that the studied wines are stabilized and do not contain viable yeast cells. Thus alcoholic fermentation will not continue in the studied wines.
For colour analysis we studied the transmittance spectra. These spectra of different sorts of red wine from Valea Calugareasca area are presented in figure 1.

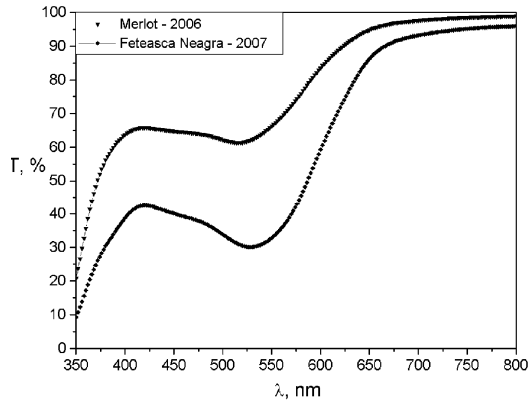

Figure 1. The transmittance spectra for Feteasca Neagra and Merlot

Using the data from these spectra, we calculated the colour coordinates of wine (x, y) and its brightness. Based on the

dominant wavelength (λ), we objectively determined the colour of wine (Table 1). We noticed that the colour of Feteasca Neagră – 2007 is red brick, while the colour of Merlot – 2006 is intense red. The sample of Feteasca Neagra had a lighter colour due to its faster evolution.

To establish the parameters of composition defining wines quality and detect any falsification of them, we carried out some analyses on key components in wine. Thus, for each wine we determined: alcoholmeter titer, relative density, total acidity, contents of methanol, glycerol, acetaldehyde, SO_2 and antocyanins.

Table 1. The colour coordinates and brightness for red wine (Valea Calugareasca area)

The colour coordinates	***x***	***y***	***Y (brightness), %***	***dominant λ, nm***
Merlot - 2006	0.3331	0.3155	70.86	597
Feteasca Neagra - 2007	0.3069	0.3774	94.30	585

To determine the methanol or citric acid content in wines, we traced the calibration curves shown in figures 2 and 3.

The absorbance of wine samples was reported in the calibration curve. The concentration of methanol, (expressed in mg/l of wine - diluted with water to 5% vol. alcohol) and the content of citric acid were determined respectively.

The characteristics of samples, obtained by chemical analysis, are presented in table 2. The values of the alcoholmeter titer (>10.5% volume) show that the two wines can be placed in the category of superior wines.

We have noticed very low volatile acidity and normal values for total acidity and fixed acidity.

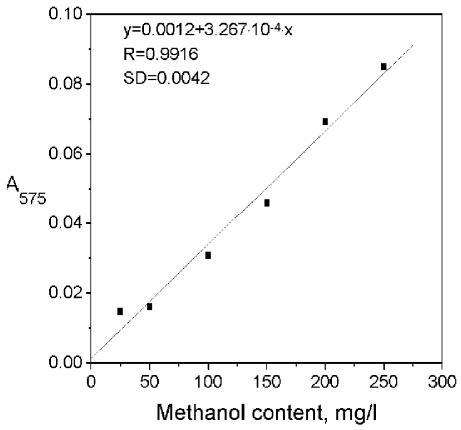

Figure 2. The calibration curve for methanol

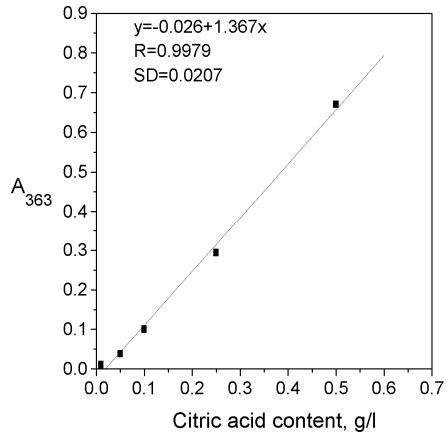

Figure 3. The calibration curve for citric acid

The content of citric acid in wine Merlot (2006) fits within acceptable limits (up to 1g/l) to correct defficient acidity of wine, while Feteasca Neagra (2007) samples show an unusual value for a quality wine produced in the Valea Calugareasca area.

The presence of free metatartric acid was not detected in the two red wines from Valea Calugareasca area, as demonstrated by the absence of any lamellar precipitate in the centrifuge tube. In addition, the values of total sugar are normal in semi-dry wines whereas the anthocyanins content correlated with the value of the colouring intensity comply with the normal range of red wines.

Table 2.
Chemical characteristics of some red wines (Valea Calugareasca area)

Analysis	***Merlot - 2006***	***Feteasca Neagra - 2007***
Alcoholmeter titter total, %	11	10.5
Total acidity, mechiv/liter	60	74
g/l tartric acid	4.5	5.55
g/l sulphuric acid	2.94	3.63
Volatile acidity, mechiv/liter	2.5	3.6
g/l sulphuric acid	0.12	0.18
g/l acid acetic	0.15	0.22
Fixed acidity, mechiv/liter	57.5	70.4
g/l sulphuric acid	2.82	3.45
g/l tartric acid	4.31	5.28
Citric acid, g/l	0.87	1.2
Ionic acidity/real pH	3.76	3.75
Total SO_2, mg/l	192	214
Total sugar, g/l	10	7.9
Antocyanins, mg/l	109	241
Glycerol, g/l	12	8.3
Methanol, mg/l	25	360
Acetaldehyde, mg/l	120	155

Conclusions

The CIE-Lab - 76 method facilitates understanding of the correspondence between visual impression of wine colour and numerical expression of chromatic parameters of wines. The chromatic characteristics are normal for wines from this area and these years.

The microbiological stability of the studied wines demonstrates a good makewine process.

The characteristics obtained from chemical analysis are normal for these wines, but do not present the typicity of the Valea Calugareasca area. This might be due to the technological process.

It is necessary to carry out more experiments, on several kinds of wines from this area, produced in different years, to perform a database that contains the *fingerprint* for each authentic wine from Valea Calugareasca.

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