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# Optical methods for tracing the kinetic changes of red wines during technological processes

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It is a well-known fact that prior to bottling wine is under permanent changes as a "living organism". While kept in oak wood tuns its physical chemical properties change during the technological processes. In the present research we study two types of red wines from the Varna region, Cabernet Franc and Pinot Noir, year 2017. Samples were picked up in December 2017 and February 2018.

The objectives of the present research are to trace the kinetics of physical chemical properties during storage under special conditions in wooden oak tuns. Spectrometric methods are used to determine the contents of anthocyanin and color parameters, mass spectrometry to estimate the quantity of Cu, the content of polyphenols was assessed and the antioxidant activity of the samples was measured using ABTS and DPPH methods. Using methods of applied photonics, fluorescence spectra for excitation of 285 nm were measured.

It has been established by both radical scavenging methods that as storage duration increases so does the wines' antiradical activity that measured using ABTS being higher. Wine of the sort Cabernet Franc exhibited a higher antioxidant activity. Lightness decreases with time being higher for the Pinot Noir wine. The content of the polyphenols decreases while that of anthocyanins increases. From the data obtained for Cu is seen that the element is in very small quantities, which is indicative of ecologically pure samples.

**Keywords:** color, red wine, fluorescence, antioxidant activity

## INTRODUCTION

The contents of wine varies over a broad range and it contains sugars, acids phenols and non-organic components. The content depends on the sort of grapes, type of soil, climatic conditions, ripeness degree and the production technology. The indicators of grapes that influence most strongly the individual characteristics of the wine are the fermenting sugars, the titratable acids, the pH of the grapes juice, the contents of general phenol compositions and the concentration of aromatic components [1-2]. During wine production, apart from the grapes quality, an essential role is played by technological factors such as the strains of wine yeast, the process of alcohol fermentation, prevention from oxidation, the formation and storage of the produced wine [3-5].

Apart from polyphenols such as catechin and epicatechin, flavanols (quercetin, rutin, myicetin), phenol acids (gallic, caffeic and p-coumarin acids), wine contains other fluorescing molecules as vitamins anaminoacids. Phenol compositions play important role on the sensor qualities of wines such as color and taste and have a positive effect on health [6-8]. These components are important because of their proven bactericidal effect [9]. The content of polyphenols in grapes is different for the different sorts of grapes. They play an important role for the quality of wine and are beneficial to human health.

It is known that climate close to the coast in Northeastern Bulgaria is more humid without higher temperatures which is a prerequisite to acquire uniform maturity of grapes and the production of pleasant flavors. It is also known that due to the lower annual temperature the presence of phenols, tannins and coloring substances in red wines from that region is lower than the South Bulgarian regions. Therefore the main purpose of producers of red wines from the region is to create red wines with nutritional values comparable to those of Southern Bulgaria by a selection of appropriate sorts of grapes, technology and storage in suitably treated wooden barrels.

The objective of the present work is to trace the kinetics of two types of red wines in different stages

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of their technological maturity and to compare with red wines from Southern Bulgaria.

## MATERIALS AND METHODS

### *Samples*

Two brands of wine made from different sort of grapes were studied:

- "Pinot Noir", year 2017, a red dry wine produced from Pinot Noir grapes sort, found in the region of Varna, maturing in oak barrels.
- "Cabernet Franc", year 2017, a red dry wine produced from Cabernet Franc grapes sort from the Varna region.

For each of the above brands are taken two samples in the course of its technological maturation - in December and February, correspondingly.

### *Methods:Mmasurement of the color characteristics*

Color parameters are determined without dilution of the sample in cuvette of 2 mm thickness by using the Lovibond PFX 880 instrument (Tintometer Limited, UK). Parameters, such as $C_{ab}$ and $h_{ab}$ are determined by the formula

$$C = \sqrt{a^2 + b^2} \quad (1)$$

$$h_{ab} = \arctan\left(\frac{b^*}{a^*}\right) \quad (2)$$

To obtain values for the parameters (color intensity, hue) providing a possibility to evaluate the quality of the wine, it is of essential importance the measurement of absorption spectra of the samples and their color parameters in SIE Lab colorimetric system. Using the above methods by analysis of the following indicators:

- Color intensity T- method of Sudraud [10]
- Anthocyanins – method of P. Ribereau-Gaylon and Stonestreet [10]

### *Spectral measurements*

The measured spectral coefficients of the optical density at 420 nm, 520 nm, 620 nm are related to the presence of the anthocyanins and phenolic compositions, as well as the blue component, for young wines [11]. The measurements were carried out with a BIM 6002 -01 Brolight (200nm to 900 nm, 1 nm resolution) using a Czerny-Turner scheme. The fluorescence spectra of the samples under study were obtained with the same spectrophotometer at excitation wavelength 265 nm and 300 nm.

The total quantity of the polyphenols is determined by the method of Singleton and Rossi [12] abd the maximum absorption at 765 nm measured with the Brolight BIM 6002 -01 spectrometer was used. The total quantity of polyphenols is expressed in milligramme-equivalent gallic acid.

Determination of the antioxidant activity is performed in two methods, estimating different aspects of the reduction activity of the samples:

(a) DPPH method, which is considered to estimate the quantity of antioxidants, which realize its activity, by hydrogen donor properties (HAT) [13] and (b) ABTS method using which are estimated basically components showing its activity through electron donor properties (SET) [14].

## RESULTS AND DISCUSSION

As first step the fluorescent spectra were obtained for each of stages of both brands of wine (Cabernet Franc and Pinot Noir) for excitation wavelengths 265 nm and 300 nm. The results are presented in Fig. 1 and 2.

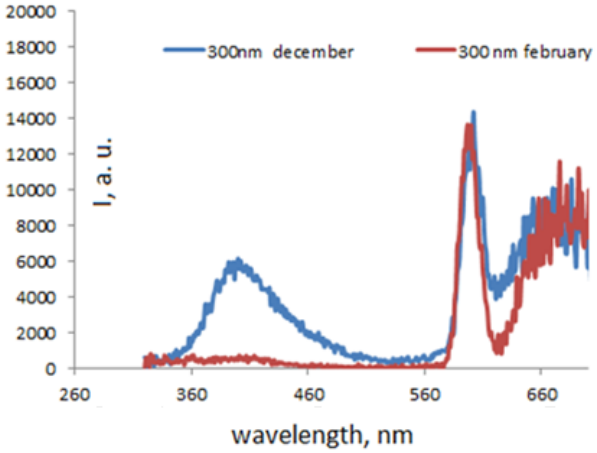


**Fig. 1.** Fluorescence spectra of Cabernet red wine excited at 300nm.

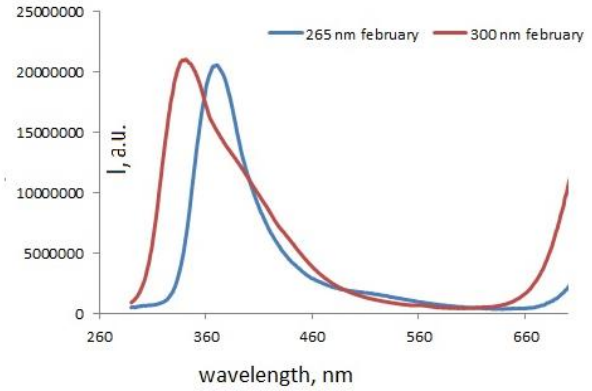


**Fig. 2.** Fluorescence spectra of Pinot Noir red wine excited at 265nm and 300 nm.

It is seen from Fig. 1 that at the excitation wavelength 265 nm and 300 nm an intensive peak in the 340nm to 365 nm for both brands of red wines for the February samples is observed. According to data from literature this peak is associated with anthocyanins [15]. The result is also confirmed by the study of the kinetics on the contents of the anthocyanins using the spectroscopic method (Table

1). In the second stage, a maximum in the Cabernet Franc sample at 530 nm associated with riboflavin [16] was observed. At the excitation wavelength of 300 nm both brands of wine exhibit a maximum around 365 nm related to the photocatechins [17]. The characteristic fluorescence peaks of t-resveratrol around 390 nm for an excitation wavelength of 300 nm in the first stage of the kinetic changes was observed for the Cabernet Franc wine [18].

The next experiments concerned evaluation of the anti-radical potential in stable free radicals containing systems. The results for the antioxidant activity of the studied samples were obtained in the presence of the free radicals ABTS and DPPH and are represented in Fig. 3.

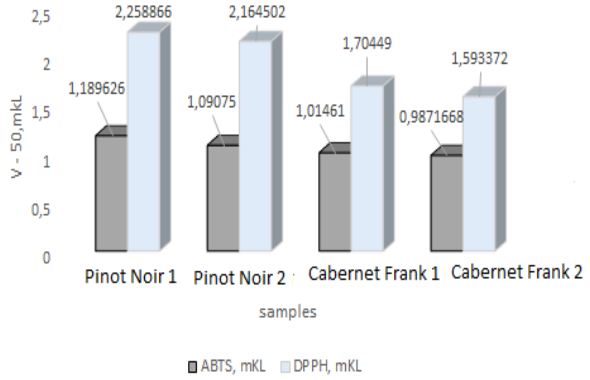


**Fig. 3** Comparison of the V-50 values estimated from the concentration-AOA dependences determined using the ABTS and DPPH assay for wine samples from Cabernet Franc and Pinot Noir obtained during the first stage of their storage.

For all samples the antioxidant potential in the model system with ABTS radical is higher compared to that with DPPH. The differences in the volume V-50 for Pinot Noir red wine is twice larger according to both methods. This means that the wines contain much more components which exhibit antioxidant activity through SET mechanism, than components showing its activity through the HAT mechanism. The dependencies shown that for the Pinot Noir, the scavenging capacity was realized predominately through the SET mechanism, because effect registered by ABTS is twice larger than the effect in the DPPH system (HAT mechanism). With the increase of storage time in oak barrels antioxidant activity increases weakly.

In order to obtain additional information and possible explanation concerning the observed changes in the AOA the anthocyanins and total phenol content of the wines samples are determined and presented in table 1. An increase of contents of anthocyanins is being observed which could be related to the observed weakly increase of antioxidant activity with the increase of storage time.

During storage time a loss of the content of polyphenols was observed [19]. Fermentation decreases the contents of polyphenol acids. The decrease of the total phenolic content in samples of Pinot Noir is weak, while for theose of Cabernet Franc decreases about 6 times. The weak decrease in the Pinot Noir can be associated with the storage in oak barrels. In the case of storage of wine and high-grade alcohol beverages in wooden barrels, the content of phenolic compositions decreases weakly for dried wood and is comparatively higher in the case non-dried wood made of winter oak and Blagun [20].

**Table 1** Kinetic change of anthocyanins and total.

| Samples | Anthocyanins, mg MAG/L | Anthocyanins, mg CYG/L | Total polyphenol content, mg GA/L |
|---|---|---|---|
| Pino Noar 1 | 61.65 ± 1.26 | 58.45 ± 2.23 | 218.70 ± 9.23 |
| Pino Noar 2 | 84.55 ± 3.29 | 80.16 ± 1.67 | 213.26 ± 6.34 |
| Cabernet Fran 1 | 127.70 ± 5.67 | 121.07 ± 11.23 | 291.52 ± 7.23 |
| Cabernet Fran 2 | 184.95 ± 4.65 | 175.34 ± 9.34 | 31.65 ± 3.45 |

The second sample of red wine of the Cabernet Franc contains a higher quantity of anthocyanins compared to the same sort of wine from Harmanli as determined in other studies of ours 166.5 mg MAG/l. Although the North-Eastern Black Sea region is known for its advantages to produce high quality white wines, it may be a producer of red wine using appropriate technology and a selection of the grapes sorts. The Pinot Noir red wine contains 12 times more anthocyanins compared to the Cabernet Franc from the Stara Zagora region. The sample possesses a total polyphenol content of about 213 mg/l, which is comparable with that in a red currant compote 239 mg/l and of the Syrah red wine – 243 mg/l.

Fig. 4 shows the color parameters at different moments of the samples in the SIELab colorimetric system.

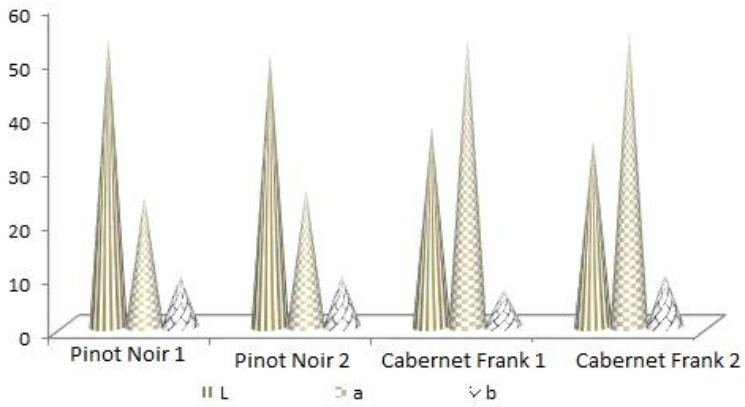


**Fig. 4.** Kinetic processes of the color parameters in the SIELab colorimetric system.

In both brands of red wines we observe a decrease of the lightness at different stages of fermentation. The Pinot Noir red wine samples exhibit a twice higher lightness compared to those of the Cabernet Franc. In all samples there exists a blue component of 9-10 units, while the units for the red component are twice as high for the Cabernet Franc compared with those of the Pinot Noir.

## CONCLUSIONS

It can be concluded that:

- For all samples the antioxidant potential in the model system with ABTS radical is higher compared to that with DPPH. During storage time a loss of the content of polyphenols was observed.
- In all samples a blue component is 9-10 units, while the units for the red component are twice as high for the Cabernet Franc compared with those of the Pinot Noir.
- The North-Eastern Black Sea region may be a producer of quality red wine using appropriate technology and a selection of the grapes sorts.

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