# DETERMINATION OF TITRATABLE ACIDITY IN WHITE WINE 

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Abstract: The amount of titration acid in must is in the largest number of cases with in the range $5.0-8.0 \mathrm{~g} / \mathrm{dm}^{3}$. Wines, as a rule, contain less acids than must, and according to Regulations, titratable acidity is in the range of 4.0-8.0 $\mathrm{g} / \mathrm{dm}^{3}$ expressed in tartaric acid, because a part of tartaric acid is deposited in the form of salts (tartar or argol) during alcohol fermentation. For wines that contain less than $4 \mathrm{~g} / \mathrm{dm}^{3}$ of titratable acids there arises a suspicion about their origin, that is, that during the preparation some illegal acts were done.

Because of that, the aim of this paper is to determine titratable acidity in white wine, using standard methods of determination, which are compared with the results received by potentiometric titration using ion-selective electrode.

According to the received results it can be seen that wine titration with indicator gives sufficient reliable values of wine titration acidity. However, as potentiometric titration at pH value 7.00 is more reliable and objective method, the values of titratable acids content in wine, expressed through tartaric acid, are given according to this result.

The analysis of differential potentiometric curves shows that these curves can give us an answer to the question of the presence of a larger amount of other nonorganic substances, which have already existed in wine. However, none of the used methods gives absolutely reliable answer what substances are present in analysed samples.

Key words: white wine, neutralization method, potentiometry, potentiometric curves, titratable acidity, buffer capacity.

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## Introduction

The acid content in wine is of great significance for the preservation and sensory characteristics of wine. The acid amount in must and wine can vary in pretty wide ranges, depending on grape variety, ripeness degree, climatic conditions during ripening, type of the soil, vineyard position, phyto-sanitary condition of grapes, applied agro-technical and ampelotechnical measures, way of grape processing, conditions according to which alcohol fermentation was done, wine storage and standing (Radovanović, 1986).

In wine there are a great number of organic acids, even more than 40 , which differ in origin. Some have been a component of grapes and must (tartaric, malic, citric acid), while the other represent intermediate products or final products of alcohol fermentation (succinic, 2-ketoglutaric, 2-dimethylglicerine acid, and hexane, octane and decane acids) (Official Gazette of FRY, 2002; Official Gazette of SM, 2003).

If grapes were overtaken by grey mould (Botrytis cinerea), then some acids like galacturonic, glucoronic, slime and hydroxy-glutaric acids can be found in wine in the increasing amount. During alcohol fermentation there arise a certain amount of vaporised acids (most common is acetic acid), whose content in the process of wine preservation increases more or less. In wine there are amino acids in the amount of a few hundred milligrams to over one gram, which are significant as of wine aroma precursors. Phenol-carbonic acids are also present in a smaller amount and they influence wine sensory characteristics (taste, colour) (Jović, 2003).

No matter if acids are present in a free state or bounded in the form of its salts, the wine acidity can be characterised by the following parameters: titratable acidity (titration acidity), actual or real acidity ( pH value) and puffer capacity.

Because of that, the aim of this paper is to determine titration acidity in white wine, using standard methods of determination, which are compared with the results received by potentiometric titration using an ion-selective electrode.

## Theoretical Aspects of Titratable Acidity Determination

## Titratable Acidity

Acids are very important components of wine that to a larger degree determine its quality. Basic acids that exist in wine are tartaric acid and its salts, and malic acid and its salts. Among these acids in wine there can be also found acetic, succinic, citric, lactic acid and their salts. Dissociation constant (acidity) of acids present in wine is shown in Table 1.

T a b. 1. - The aqueous dissociation constants for some wine constituents

| Acid | $\mathrm{pK}_{\mathrm{al}}$ | $\mathrm{pK}_{\mathrm{a} 2}$ | $\mathrm{pK}_{\mathrm{a} 3}$ |
| :---: | :---: | :---: | :---: |
| Tartaric | $3.07{ }^{1}$ | $4.39{ }^{1}$ |  |
| Malic | $3.48{ }^{1}$ | $5.10{ }^{1}$ |  |
| Lactic | $3.89{ }^{1}$ |  |  |
| Succinic | $4.21{ }^{1}$ | $5.64{ }^{1}$ |  |
| Sulfurous | $1.80{ }^{2}$ | $7.20{ }^{2}$ |  |
| Citric | $3.06{ }^{3}$ | $4.74{ }^{3}$ | $5.40{ }^{3}$ |
| Oxalic | $1.19{ }^{3}$ | $4.21{ }^{3}$ |  |
| Glutaric | $2.47{ }^{4}$ | $4.68{ }^{4}$ |  |
| Galacturonic | $3.50{ }^{1}$ |  |  |
| Gluconic | $3.81{ }^{\text {1 }}$ |  |  |
| Glucoronic | $3.26{ }^{1}$ |  |  |
| Pyruvic | $2.71{ }^{1}$ |  |  |
| Ascorbic | $4.1{ }^{3}$ | $11.79{ }^{3}$ |  |
| Arginine | $2.17{ }^{3}$ | $9.04{ }^{3}$ |  |
| Proline | $1.99{ }^{3}$ | $10.60{ }^{3}$ |  |
| Aspartic | $2.09{ }^{3}$ | $3.86{ }^{3}$ | $9.82{ }^{3}$ |
| Glutamic | $2.19^{3}$ | $4.25{ }^{3}$ | $9.67{ }^{3}$ |
| Ammonia | $9.2{ }^{2}$ |  |  |
| Carbonic | $6.4{ }^{2}$ | $10.3{ }^{2}$ |  |
| Acetic | $4.78{ }^{1}$ |  |  |
| Sorbic | $4.76{ }^{3}$ |  |  |
| Phosphoric | $2.1^{2}$ | $7.2^{2}$ | $12.4{ }^{2}$ |
| Sulfuric | $-9.0{ }^{5}$ | $2.0{ }^{2}$ |  |
| Nitric | $-1.4{ }^{2}$ |  |  |
| Gallic | $4.41^{3}$ |  |  |
| Cinnamic | $4.44{ }^{6}$ |  |  |
| Hydrogen sulfide | $7.0^{2}$ | $12.9{ }^{2}$ |  |

${ }^{1}$ Usseglio-Tomasset and Bosia, 1978; ${ }^{2}$ Ayward and Findlay, 1966; ${ }^{3}$ Segal, 1976;
${ }^{4}$ Dawson et al., 1969; ${ }^{5}$ Stranks et al., 1965; ${ }^{6}$ Weast, 1977
Titratable acids represent the sum of all acids in wine, except carbonic acids $\left(\mathrm{H}_{2} \mathrm{CO}_{3}\right.$ or $\left.\mathrm{H}_{2} \mathrm{O}+\mathrm{CO}_{2}\right)$. Titratable acidity (acidity) is determined by wine titration (after removal $\mathrm{CO}_{2}$ ) till the end point of titration by a strong base and is expressed by proton number received as equivalent concentration of selected acid. In the United States the end point chosen is $\mathrm{pH}=8.20$ and the acid for reference is tartaric acid. In some other countries, for example France, the end point is $\mathrm{pH}=$ 7.00 and the reference acid is sulphuric. Titration acidity is commonly with in the range $4.0-8.0 \mathrm{~g} / \mathrm{dm}^{3}$ expressed in tartaric acid (Peynaud and Maurie, 1956; Boulton, 1980a; Boulton, 1980b).

The term titration acids is often wrongly identified with the term total acids. Titration acidity (acidity) consists of acids that can be titrated by the strong base solution and these are their free carboxylic functions $(-\mathrm{COOH})$. However, a part of wine acids has carboxylic functions totally or partially neutralised by
cations (potassium, sodium and/or calcium). The term total acids becomes correct if wine is first put through colon with ion-exchange resin and all carboxylic functions are released, and then their neutralization is started to with a strong base (Vine and Harkness, 1997).

## Active Acidity or pH Value of Wine

Acetous taste of wine doesn't depend much of acid content but of the strength of most present acids. Acid strength is closely connected with hydrogen ion concentration. If acid gives more hydrogen ions by dissociating, it is more acetous. The strongest organic acid in wine, tartaric acid, is only partially ionized to two $\mathrm{H}^{+}$ions and tartrate anion $\left(\mathrm{C}_{4} \mathrm{H}_{4} \mathrm{O}_{4}{ }^{2-}\right)$. Besides ionizing, non-ionizing forms of tartaric acid also exist in wine. Tartaric acid is also present in the form of its salts, with the most important monopotassium-tartrate (tartar or argol), which is dissociated in water solution, to hydrogen and potassium and tartrate ion. If 1 mol of different acids is dissolved in $226 \mathrm{dm}^{3}$ of water, then their dissociated part would be in the percentage as follows: for tartaric $39.4 \%$, citric $36.6 \%$ and malic acid $27.1 \%$. The pH values of must are in the range of $2.80-3.80$ and they are regularly lower than in wine. Wine with enough acids usually has pH values lower than 3.50 , while in wine that doesn't have enough acids the values rise even to 4.00 . Wine has a fewer acids than must considering that part of tartaric acid is deposited in the form of tartar (or argol), as well as for possible lactic fermentation of malic acid (Boulton, 1980c).

The acidity of wine, the pH in particular, plays an important role in many aspects of winemaking and wine stability. The ability of most bacteria to grow, the solubility of the tartarate salts, the effectiveness of sulphur dioxide, ascorbic acid, the enzyme additions, the solubility of proteins and effectiveness of bentonite, the polymerization of the color pigments, as well as oxidative and browning reactions are all influenced by the wine pH . The titratable acidity is an important parameter in the sensory of evaluation of finished wines. This and the pH value are also important factors in aging reactions (Leonard and Hodges, 1973; Radovanović, 1986).

## Buffer Capacity

The property of a wine that resists changes in pH during acid or base changes is referred to as the buffer capacity or buffer index. It is defined as the number of protons per liter that are needed to shift the pH by one unit, and it can be defined in either the acidic or basic direction. Numerically, it is the inverse slope of the titration curve in the region of the pH of the wine. It is important to understand because it will explain the changes in pH that result from any change in acidity in wines.

The units of the buffer capacity are moles $\mathrm{H}^{+}$ions (or $\mathrm{OH}^{-}$ions) per liter per pH unit $(\mathrm{M} / \mathrm{L} / \mathrm{pH})$ but because of the values of buffer capacity in wines, it is common to express them in millimolar terms and these are generally in the range of 35 to $50 \mathrm{mM} / \mathrm{L} / \mathrm{pH}$ unit, although they can be as low as 25 and as high as 60 under certain conditions.

The buffer capacity is also a function of pH and is related to the proximity of the mixture pH to the $\mathrm{pK}_{\mathrm{a}} \mathrm{s}$ of the component acids as well as their concentrations. It has two components at pH below 7.00 one due to water and the other due to the acids. The equation for predicting the buffer capacity, $\beta$, of a monoprotic acid in solution is (Butler, 1964):

$$
\begin{equation*}
\beta=\frac{\left[H^{+}\right]}{K_{w}}+2,303 \cdot \frac{\left[H^{+}\right] \cdot K_{a} \cdot c}{\left(\left[H^{+}\right]+K_{a}\right)} \tag{1}
\end{equation*}
$$

where $K_{\mathrm{a}}$ is the dissociation constant of the acid; $c$ is the concentration of the acid in all forms; and $K_{\mathrm{w}}$ is the ionization constant of water $\left(1 \cdot 10^{-14}\right)$. It can be seen that the buffer capacity of the acid is greatest when $\left[\mathrm{H}^{+}\right]$equals $K_{\mathrm{a}}$ (or when the pH is equal to the $\mathrm{pK}_{\mathrm{a}}$ of the acid). This relationship can be used for mixtures of monoprotic acids and many diprotic acids (by considering them to be made up of two monoprotic acids). Unfortunately, this is not true for most of the diprotic acids found in wines because the second dissociation is not completely independent of the first.

The commonly used Henderson-Hasselbach equation (Segal, 1976; Rajković, 2007):

$$
\begin{equation*}
\mathrm{pH}=\mathrm{pK}_{\mathrm{a} 1}+\log \frac{[\text { first ionization form }]}{[\text { undissociated acid }]} \tag{2}
\end{equation*}
$$

and

$$
\begin{equation*}
\mathrm{pH}=\mathrm{pK}_{\mathrm{a} 2}+\log \frac{[\text { second ionization form }]}{[\text { first ionization form }]} \tag{3}
\end{equation*}
$$

is not valid when the $\mathrm{pK}_{\mathrm{a}} \mathrm{s}$ of the diprotic acids less than approximately two pH units apart and there is interaction between the first and second dissociated acid forms. This results in an equilibrium in which the intermediate ion form begins to dissociate at pH values where the undissociated acid is also present. Under these conditions, there is no intermediate pH range at which only two species are present and alternative expressions must be used to determine the buffer capacity and acid ionization. Such an expression for the buffer capacity is given by (Butler, 1964):

$$
\begin{equation*}
\beta=\frac{\left[\mathrm{H}^{+}\right]}{\mathrm{K}_{\mathrm{w}}}+2.303 \cdot \mathrm{c} \cdot \mathrm{~K}_{\mathrm{a} 1} \cdot\left[\mathrm{H}^{+}\right] \cdot \frac{\left(\left[\mathrm{H}^{+}\right]^{2}+4 \cdot \mathrm{~K}_{\mathrm{a} 2} \cdot\left[\mathrm{H}^{+}\right]+\mathrm{K}_{\mathrm{a} 1} \cdot \mathrm{~K}_{\mathrm{a} 2}\right)}{\left(\left[\mathrm{H}^{+}\right]^{2}+\mathrm{K}_{\mathrm{a} 1} \cdot\left[\mathrm{H}^{+}\right]+\mathrm{K}_{\mathrm{a} 1} \cdot \mathrm{~K}_{\mathrm{a} 2}\right)} \tag{4}
\end{equation*}
$$

where $K_{\mathrm{a} 2}$ is the second ionization constant and the other terms are as defined in Equation (1). It can be seen that the buffer capacity is strongly pH -dependent. The expression for a mixture of two monoprotic acids reduces to this form only when the $K_{\mathrm{a} 2}$ is less than $5 \%$ of the $K_{\mathrm{a} 1}$, or expressed another way, when the $\mathrm{pK}_{\mathrm{a}} \mathrm{s}$ differ by more than 1.98 .

The dissociation curve for tartaric acid is shown in Figure 1.


Fig 1. - The dissociation diagram for tartaric acid in wine.
Sulfur dioxide, however, does obey the Henderson-Hasselbach equations, since its $\mathrm{pK}_{\mathrm{a}} \mathrm{S}$ are more than 5 units apart.

## Buffer Capacity Curves

The buffer capacity terms of different acids in a mixture are additive and the buffer capacity of wines can be estimated from the acid concentrations and the pH . Typical buffer capacity curves for a wine is shown in Figure 2. The values below pH of 2.50 are due to water alone (the two peaks are due to higher buffer capacity in the region of the 3.00 to 3.40 because of the first ionization of tartaric and malic acids). The buffer capacity is highest in this range, falling off as the pH moves away in either direction (increase acidity).


Fig. 2. - The effect of pH on the buffer capacity in wine.

## Materials and Methods

There are some adequate chemical methods for determination of some acids existing in wine. However, determination of every acid itself is a long and complicated process, so in practice titration wine acidity is determined the method of neutralization. In this paper titratable acidity in white wine was determined by:
a) wine titration with indicator bromthymol blue,
b) titration with indicator phenolphthalein, and
c) potentiometric titration.

Examined wines: sample 1. Banatski rizling (manufacturer: Vršački vinogradi, Vršac, table dry white wine with geographic origin, content of alcohol - 11.30 vol.\%); sample 2. Fruškogorsko belo vino (manufacturer: Navip, Beograd, table dry white wine without geographic origin, content of alcohol 11.40 vol.\%); sample 3. Ključka graševina (manufacturer: Navip, Beograd, quality dry white wine, content of alcohol - 11.50 vol.\%); sample 4. Palićko belo (manufacturer: Vršački vinogradi, table dry white wine with geographic origin, content of alcohol - 11.30 vol.\%); sample 5. Rizling Rajnski (wine which is produced at the "Radmilovac" site, experimental station of the Faculty of Agriculture, Zemun).

Reagents: Sodium carbonate as primary standard solution of 0.05 $\mathrm{mol} / \mathrm{dm}^{3}$ concentration; Hydrochloric acid as standard solution of $0.1 \mathrm{~mol} / \mathrm{dm}^{3}$
concentration; Potassium hydroxide as standard solution of $0.25 \mathrm{~mol} / \mathrm{dm}^{3}$ concentration;

Indicators: Bromthymol blue: 0.4000 g bromthymol blue was measured on analytic balance and dissolved in a small volume of distilled water, and then quantitatively put into $100 \mathrm{~cm}^{3}$ measuring dish. Then $20.00 \mathrm{~cm}^{3}$ of $96 \%$ alcohol and $7.40 \mathrm{~cm}^{3}$ solution of sodium hydroxide of $0.1 \mathrm{~mol} / \mathrm{dm}^{3}$ concentration was added; Phenolphtalein: 1.0000 g of solid substances was measured on analytic balance and was dissolved in $60 \mathrm{~cm}^{3}$ of $96 \%$ alcohol solution in $100 \mathrm{~cm}^{3}$ measuring dish; Methyl orange: 0.1000 g of solid substances was measured on analytic balance and quantitatively dissolved in distilled water in $100 \mathrm{~cm}^{3}$ measuring dish (Rajković and Novaković, 2005).

Sodium carbonate solution was prepared in order to standardize hydrochloric acid solution. For standardization $10.00 \mathrm{~cm}^{3}$ of sodium carbonate solution was pipetted, two drops of methyl orange indicator and small quantities of distilled water were added. Such prepared solution was titrated by hydrochloric acid solution till changing the indicator colour from yellow to first orange. Standardization of hydrochloric acid solution was developed according to the following reaction (Rajković and Novaković, 2005):

$$
2 \mathrm{HCl}_{(\mathrm{aq})}+\mathrm{Na}_{2} \mathrm{CO}_{3(\mathrm{aq})} \rightarrow 2 \mathrm{NaCl}_{(\mathrm{aq})}+\mathrm{CO}_{2(\mathrm{~g})}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})}
$$

Concentration of hydrochloric acid solution $(\mathrm{HCl})$ is calculated in the following way:

$$
c(\mathrm{HCl})=2 \cdot \frac{c\left(\mathrm{Na}_{2} \mathrm{CO}_{3}\right) \cdot V\left(\mathrm{Na}_{2} \mathrm{CO}_{3}\right)}{V_{\mathrm{s}}(\mathrm{HCl})}
$$

After hydrochloric acid solution standardization, potassium hydroxide solution standardization was done. In $250 \mathrm{~cm}^{3}$ erlenmeyer $20.00 \mathrm{~cm}^{3}$ of acid solution was pipetted, and two drops of indicator phenolphthalein and small quantities of distilled water were added. Such prepared solution was titrated by potassium hydroxide solution till changing the indicator colour from colourless to first pink. Standardization of potassium hydroxide solution by hydrochloric acid solution was developed according to the following chemical equation:

$$
\mathrm{KOH}_{(\mathrm{aq})}+\mathrm{HCl}_{(\mathrm{aq})} \rightarrow \mathrm{KCl}_{(\mathrm{aq})}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})}
$$

Concentration of base solution is calculated in the following way:

$$
c(\mathrm{KOH})=\frac{c(\mathrm{HCl}) \cdot V(\mathrm{HCl})}{V_{\mathrm{s}}(\mathrm{KOH})}
$$

Determination of titratable wine acidity with bromthymol blue indicator was done in the following way: $20.00 \mathrm{~cm}^{3}$ of sample was pipetted for the analysis,
$2.00 \mathrm{~cm}^{3}$ of working solution of indicator was added and titrated by the solution of potassium hydroxide till changing the indicator colour from yellow to first green. Three titrations were done and average consumption of the base solution was calculated (Daničić, 1984). Titration with indicator phenolphthalein was done in the same way, the colour changing from colourless to first pink (Rajković and Novaković, 2005).

Apparatus for potentiometric titration consisted of pH -meter (Eutech, Netherland) and magnetic stirrer. In a $100 \mathrm{~cm}^{3}$ glass $20.00 \mathrm{~cm}^{3}$ of sample was pipetted, magnetic nucleus was put in and a combined pH electrode for the analysis was placed in the solution. Titration was done by the solution of potassium hydroxide with stirring by magnetic agitator, where titration solution was added in $0.2 \mathrm{~cm}^{3}$ aliquots. After every adding of the potassium hydroxide solution, pH value of the solution was observed (Rajković, 2007).

## Results and Discussion

Determination of titratable acidity of wine with indicator or by potentiometric is based on neutralization of all acids and their acid salts, by potassium hydroxide solution. According to consumption of the base solution, titratable acidity is calculated. Potassium hydroxide is used for neutralization of all substances in wine that have acid character, so the amount of total acids in wine is expressed as the mass of tartaric acid, as for the wine quality this acid is one of the most important.

Presuming that neutralization of tartaric acid and its acid salts has been done by the following reactions:

$$
\begin{gathered}
2 \mathrm{KOH}_{(\mathrm{aq)}}+\mathrm{H}_{2} \mathrm{C}_{4} \mathrm{H}_{4} \mathrm{O}_{6(\mathrm{aq)}} \rightarrow \mathrm{K}_{2} \mathrm{C}_{4} \mathrm{H}_{4} \mathrm{O}_{6(\mathrm{aq)}}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})} \\
\mathrm{KOH}_{(\mathrm{aq)}}+\mathrm{HC}_{4} \mathrm{H}_{4} \mathrm{O}_{6(\mathrm{aq)})} \mathrm{KC}_{4} \mathrm{H}_{4} \mathrm{O}_{6(\mathrm{aqq})}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})} \\
\mathrm{KOH}_{(\mathrm{aq)}}+\mathrm{KC}_{4} \mathrm{H}_{4} \mathrm{O}_{6(\mathrm{aq})}^{-} \rightarrow \mathrm{K}_{2} \mathrm{C}_{4} \mathrm{H}_{4} \mathrm{O}_{6(\mathrm{aq})}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})}
\end{gathered}
$$

Mass of tartaric acid is calculated in the following way:

$$
m\left(\mathrm{H}_{2} \mathrm{C}_{4} \mathrm{H}_{4} \mathrm{O}_{6}\right)=\frac{1}{2} \cdot c(\mathrm{KOH}) \cdot V(\mathrm{KOH}) \cdot M\left(\mathrm{H}_{2} \mathrm{C}_{4} \mathrm{H}_{4} \mathrm{O}_{6}\right)
$$

As the content of tartaric acid is expressed in $\mathrm{g} / \mathrm{dm}^{3}$ the above equation should be multiplied by factor 50 :

$$
m\left(\mathrm{H}_{2} \mathrm{C}_{4} \mathrm{H}_{4} \mathrm{O}_{6}\right)=\frac{1}{2} \cdot c(\mathrm{KOH}) \cdot V(\mathrm{KOH}) \cdot M\left(\mathrm{H}_{2} \mathrm{C}_{4} \mathrm{H}_{4} \mathrm{O}_{6}\right) \cdot 50
$$

The results obtained by potentiometric titration were processed with software Origin 6.1 for maths data processing.

Obtained potentiometric titration curves are shown in Figure 3.


Fig. 3. - Potentiometric titration curves

In Figure 4 differential potentiometric curves are shown.


Fig. 4. - Differential potentiometric titration curves
In Table 2 the results of measurements of real pH values of wine samples that mark concentration of free $\mathrm{H}^{+}$ions in wine are shown. Values of real pH depend from the amount of total acids and strength of their dissociation. Of carboxylic acids that often exist in wine, tartaric acid is most strongly dissociated,
malic acid less than it, and other carboxylic acids are even weaker. $\mathrm{So}, \mathrm{pH}$ values of wine samples mostly depend of the amount of tartaric acid in wine.

Concentration of $\mathrm{H}^{+}$ions, that is, pH value, is not directly proportional to the amount of total acids in wine. With increasing of total acids, concentration of $\mathrm{H}^{+}$ions, that is real pH value of wine, is not always increasing proportionally.

Tab. 2. - Real pH value of samples and titratable acidity of analysed wines expressed by the mass of tartaric acid in $1 \mathrm{dm}^{3}$ of wine

| Sample | $m\left(\mathrm{H}_{2} \mathrm{C}_{4} \mathrm{H}_{4} \mathrm{O}_{6}\right), \mathrm{g} / \mathrm{dm}^{3}$ |  |  |  |  |
| :--- | :---: | :---: | :---: | :---: | :---: |
|  |  | Bromthymol <br> blue | Phenolphtalein | Potentiometric titations |  |
|  |  |  |  | at $\mathrm{pH}=7.00$ | extract |
| Banatski rizling |  | 5.64 | 6.04 | 5.94 | 6.34 |
| Fruškogorsko belo | 3.39 | 6.64 | 7.03 | 6.79 | 6.84 |
| Ključka graševina | 2.99 | 6.73 | 7.08 | 6.93 | 7.33 |
| Palićko belo | 3.53 | 5.20 | 5.55 | 5.65 | 6.00 |
| Rizling Rajnski | 3.24 | 9.02 | 9.11 | 10.00 | 10.40 |

According to the results shown in Table 2, it can be seen that Ključka graševina has the highest real pH value, while Rizling Rajnski has the highest content of total acids. That means that Ključka graševina mostly contains tartaric acid, while the content of other acids in this wine is very small. On the other hand, wine Rizling Rajnski has a small amount of tartaric acid and high amount of other acids (Daničić, 1987).

In Table 3 there are given values of potassium hydroxide solution volume in the end point of titration with bromthymol blue indicator, that is, phenolphthalein. In the same table values of potassium hydroxide solution volume determined according to potentiometric titration, and which were read in two different ways are also given. Namely, during the potentiometric determination of wine acidity, titration with base solution is done till reaching solution pH values of 7.00 (Boulton et al., 1996). Then, titration is stopped and consumption of the base solution is read (Daničić, 1987). In this paper titration of wine samples was done until after the end point of titration. In this way all substances in wine samples that have acid character were neutralised by base solution. Other values of potassium hydroxide volume consumed in the end point of titration were read according to highest rise in differential potentiometric curves.

According to the results shown in Table 3, significant differences in determination of titration acidity in wine by potentiometric titration and bromthymol blue titration can be observed. Although in practice the common method for determination of titratable acidity in wine is titration with bromthymol
blue (Prenesti et al., 2004), the process of potentiometric titration is more reliable and precise.

T a b. 3. - Volume of sodium hydroxide solutions in the end point

| Sample | $V(\mathrm{KOH}), \mathrm{cm}^{3}$ |  |  |  |  |
| :--- | :---: | :---: | :---: | :---: | :---: |
|  |  | Bromthymol blue | Phenolphtalein | Potentiometric titations |  |
|  |  |  |  | extract |  |
| Banatski rizling | 5.70 | 6.10 | 6.00 | 6.40 |  |
| Fruškogorsko belo | 6.70 | 7.10 | 6.85 | 6.90 |  |
| Graševina | 6.80 | 7.15 | 7.00 | 7.40 |  |
| Palićko belo | 5.25 | 5.60 | 5.70 | 6.05 |  |
| Rizling Rajnski | 9.10 | 9.20 | 10.10 | 10.50 |  |

In this paper it was analysed the usage of phenolphthalein as the indicator for determination of titratable acidity in wine, without previous disposal of carbon dioxide. The results from Table 3 show relatively good compatibility of these results with potentiometric titration. Compatibility of the results is present in Banatski rizling, Ključka graševina and Palićko belo. However, in the analysis of Fruškogorsko belo and Rizling Rajnski the differences in consumption of potassium hydroxide solution are significant. According to these observations, it can be concluded that wine titration with indicator can be only one of the methods for determination of titratable acidity in wine. As the method of potentiometric titration gives more reliable and objective results, the results in Table 2 calculated according to potentiometric titration at pH 7.00 are the most precise results of the analysis.

More detailed analysis of differential potentiometric curves shows the presence of small rises before and after the highest rise in curve. From common theoretical observation it is realised that every rise on differential curve corresponds to one end point of titration. In Figure 4 it can be seen that for titration of Banatski rizling there is one, while in titration of Fruškogorsko belo and Ključka graševina there are two rises that proceed to the highest rise on the curve. These rises occur in the pH value range of 5.40-6.70 and probably correspond to titration of nonorganic substances present in wine, among all to sulfur dioxide titration. Although these rises can't be seen in titration of Palićko belo and Rizling Rajnski, it can't be said that nonorganic substances are not present in wine, but that their concentration is very low.

Rises on differential potentiometric curves that occur after the highest rise correspond to pH range from 10.20 to 11.56 . These results show the content of substances in wine such as biogenic amines, amino acids (amino groups) and phenol compounds, and that have less constants of acidity than carboxylic acids present in wine. These compounds do not significantly influence total wine
acidity and, on the other hand, determination of the end point of titration for these compounds is always discussible (Durliat and Comtat, 2005; Prenesti et al., 2004). Namely, oxido-reduction and/or processes of sedimentation (as the oxidation of phenol and so) have advantage in relation to acidic-basic reactions, so they make it impossible that this part of titration curve be registered precisely and reproductively. From Figure 4 it can be seen that the presence of these compounds on titration curve cannot be registered for Ključka graševina and Rizling Rajnski. As for Palićko belo even two end points that correspond to the presence of these compounds have been registered.

The highest rise on differential titration curve for all wine samples occurs in the pH range from 7.25 to 8.70 . According to pH values, it is obvious that in this point the present acetic acid and nonorganic substances, such as carbon dioxide and sulfur dioxide are completely neutralised. As only carboxylic acids are significant for wine quality, it is obvious why in practice potentiometric determination of total acidity stops at the moment when pH values of titrated solution is 7.00 (Boulton et al., 1996).

## Conclusion

According to the shown results, it can be seen that wine titration with indicator gives sufficiently reliable values of titration acidity in wine (OIV, 2005). However, as potentiometric titration for pH value 7.00 is more reliable and objective method, values for content of total amount of acids in wine, expressed through tartaric acid, have been given according to these results. According to titratable acidity in analysed wines, all wines according to their structure correspond to Regulations about wine quality.

The analysis of differential potentiometric curves shows that these curves can give us the answer to the question if nonorganic substances, amino groups and phenols are present in wine in a larger amount, as they are always present in wine. However, neither of analysed methods gives strict answer to the question what substances are present in analysed samples. The answer to this question can be received only by the method of ionic chromatography.

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## ODREĐIVANJE TITRACIONE KISELOSTI U BELOM VINU

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> Rezime

Količina titracionih kiselina u širi se, u najvećem broju slučajeva, kreće između 5 i $8 \mathrm{~g} / \mathrm{dm}^{3}$. Vina, po pravilu, sadrže nešto manje kiselina nego šira, a prema Pravilniku, titraciona kiselost se kreće između 4,0 i $8,0 \mathrm{~g} / \mathrm{dm}^{3}$ izraženo u vinskoj kiselini, jer se deo vinske kiseline istaloži u obliku soli (streša) u toku alkoholne fermentacije. Za vina koja sadrže ispod $4 \mathrm{~g} / \mathrm{dm}^{3}$ titracionih kiselina postoji sumnja u njihovo poreklo, tj. da su prilikom njihovog spravljanja vršene nedozvoljene radnje.

Zbog toga je cilj rada bio da se izvrši određivanje titracione kiselosti u belom vinu, standardnim metodama određivanja koje su upoređene sa rezultatima dobijenim potenciometrijskom titracijom uz jon-selektivnu elektrodu.

Na osnovu dobijenih rezultata uočava se da titracija vina uz indikator daje dovoljno pouzdane vrednosti titracione kiselosti vina. Međutim, pošto je potenciometrijska titracija, pri pH vrednosti 7,00 , pouzdanija i objektivnija metoda, vrednosti za sadržaj titracionih kiselina u vinu, izraženih preko vinske kiseline, date su upravo na osnovu ovog rezultata.

Analiza diferencijalnih potenciometrijskih krivih, ukazuje da ove krive mogu pružiti odgovor na pitanje o prisustvu veće količine drugih neorganskih supstanci, koje se već nalaze u vinu. Međutim, ni jedna od ispitivanih metoda ne daje dovoljno pouzdan odgovor koje supstance su prisutne u analiziranim uzorcima, već odgovor na ovo pitanje može pružiti jedino metoda jonske hromatografije.

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