The possibility of using the potentiometric titration method to determine the antioxidant properties of wines

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Abstract. The results of study of phenolic composition, antioxidant activity and oxidation state of phenolic substances of white and red table wine materials were presented. Close correlational between the antioxidant activity of white table wine materials, the oxidation parameter of phenolic composition and the content of monomeric, oligomeric and polymeric forms of phenolic compounds were established. The correlation between antioxidant activity and oxidation parameter of phenolic substances has not been established for red wine materials. Direct effect of the oxidation state of phenolic substances in white table wine materials on their antioxidant activity was shown. The oxidation parameter of phenolic substances can be used as a criterion of assessing the antioxidant properties of white table wine materials and wines. The method of potentiometric titration may be recommended for use in processing, training and experimental analytical laboratories to assess the antioxidant activity of white table wine materials and wines.

1. Introduction

The high biological activity of grape wines is confirmed by numerous studies and depends on the total grape polyphenols contained in them, the qualitative and quantitative composition of which determines the integral antioxidant activity [1-7]. A wide range of methods for determining antioxidant activity is used in the world practice, both instrumental "in vitro" and "in vivo" methods on biological objects, including photocolorimetric, fluorimetric methods, methods based on electron paramagnetic resonance spectroscopy, chemiluminescent and voltammetric methods [7-14].

These methods are designed to determine the antioxidant activity not only in wine materials and wines, but also in environments characterized by a high content of polyphenols (alcohol extracts, polyphenol concentrates) [15, 16]. Almost all methods for determining antioxidant activity with their high accuracy, reliability and reproducibility require expensive equipment, reagents, and special training of specialists who conduct them, which leads to the search for less time-consuming and expensive ways to assess antioxidant activity for research objects with a low content of phenolic substances (0.2-1.0 g/dm³) [17, 18], which include white table wine materials and wines.

Various classes of phenolic compounds that determine antioxidant activity are characterized by the presence of hydroxyl groups that are capable of oxidation [19, 20]. The relationship between the state of oxidation of polyphenols and the values of antioxidant activity of wine materials and wines has not
yet been sufficiently studied. Therefore, the purpose of our work was to study the effect of oxidation of phenolic compounds of grape wine materials and wines on their antioxidant properties, as well as to study the prospects for using the method of potentiometric titration to assess antioxidant activity.

2. Objects and research methods.

The study material was white and red table wine materials from Rkatsiteli and Cabernet Sauvignon grapes, the preparation schemes of which provided for the use of methods that provide a variation in the content of phenolic compounds (table 1).

| No. | Sample name                                      |
|-----|-------------------------------------------------|
| 1   | Rkatsiteli in white, before pasting             |
| 2   | Rkatsiteli, in white, after pasting             |
| 3   | Rkatsiteli, 6 hours infusion of pulp, before pasting |
| 4   | Rkatsiteli, 6 hours of infusion of the pulp, after pasting |
| 5   | Rkatsiteli, 12 hours of infusion of the pulp, before pasting |
| 6   | Rkatsiteli, 12 hours of infusion of the pulp, after pasting |
| 7   | Rkatsiteli, 24 hours infusion of pulp, before pasting |
| 8   | Rkatsiteli, 24 hours of infusion of the pulp, after pasting |
| 9   | Rkatsiteli, fermentation of 2/3 sugars with ridges, before pasting |
| 10  | Rkatsiteli, fermentation of 2/3 sugars with combs, after pasting |
| 11  | Rkatsiteli, complete fermentation of sugars with ridges, before pasting |
| 12  | Rkatsiteli, complete fermentation of sugars with ridges, after pasting |
| 13  | Cabernet, red, before pasting                   |
| 14  | Cabernet, red, after pasting                    |
| 15  | Cabernet, with heating the pulp, before pasting |
| 16  | Cabernet, with heating the pulp, after pasting  |
| 17  | Cabernet, fermented with ridges, before pasting |
| 18  | Cabernet, fermented with ridges, after pasting  |

Antioxidant activity was determined on a photochemical antioxidant analyzer (Analytik Jena AG, Germany) using a chemiluminescent method, based on the phenomenon of chemiluminescence – the ability of radicals (superoxide anion radicals, hydroxyl and lipid radicals) to glow during the recombination reaction and consisting in measuring the intensity of the glow before and after the introduction of an antioxidant radical inhibitor into the system [6].

The oxidation state of the phenolic complex was evaluated by the oxidation parameter [7], which characterizes the contribution of a unit of phenolic substances to the change in redox potential. The values of the oxidation parameter were calculated based on the data obtained by the method of potentiometric titration, as well as the method for determining the mass concentration of phenolic compounds with Folin–Ciocalteu reagent [8,9] using the equation (1):

\[
    w = \frac{\Delta E_h}{C_\phi}
\]

where \( \Delta E_h \) – potential change, mV; 
\( C_\phi \) – mass concentration of the sum of phenolic substances, mg/dm 3.

The qualitative and quantitative composition of phenolic compounds was determined by HPLC using the Agilent Technologies chromatographic system (model 1100) with a diode-matrix detector (a Zorbax SBC18 chromatographic column was used to separate substances) [13].
3. Results
Comparative analysis of the obtained data showed that the mass concentration of phenolic compounds in experimental samples varied from 0.17 to 0.89 g/dm3 for white and from 1.59 to 2.04 g/dm3 for red wine materials. At the same time, the phenolic composition of white and red wine materials differed significantly. In addition to the presence of anthocyanins, red wine materials were characterized by a higher content of polymer forms of phenolic compounds (5 times compared to white ones), and oligomeric procyanidins (1.6 times) and monomeric forms of phenolic substances (2.4 times) (figure 1-2).

![Figure 1. Composition of the monomer complex of phenolic compounds in Rkatsiteli wine materials.](image)

![Figure 2. Composition of the monomer complex of phenolic compounds in Cabernet wine materials.](image)

A similar pattern was observed for certain groups of Monomeric forms of phenolic compounds (figure 3, 4). Thus, the content of flavones, flavan-3-ols, oxybenzoic and oxyeeric acids in red wine materials was 2-6 times higher than in white.

Differences in the phenolic composition were accompanied by a significant difference between the values of the antioxidant activity of white and red wine materials (figure 5, 6). The maximum value of this indicator in white wine materials did not exceed 1.74 g/dm3, while the minimum antioxidant activity for red wine materials was 8.98 g/dm3. On average, the antioxidant activity of red wine materials was 10 times higher than that of white ones.
The analysis of the potentiometric titration data showed (figure 4) that the values of the oxidation parameter in white wine materials were 0.04-0.96 mVdm3/mg, and in red – 0.062-0.10 mVdm3/mg. Higher values of the oxidation parameter, which characterizes the ability of phenolic substances to oxidize (i.e. the degree of their reduction) [15], of white wine materials in comparison with red ones indicate the predominance of reduced forms of phenolic substances in white wine materials and a greater oxidation of the components of the phenolic complex of red wine materials (more than 5 times).

**Figure 3.** Composition of the monomer complex of phenolic compounds in Rkatsiteli wine materials.

**Figure 4.** Composition of the monomer complex of phenolic compounds in Cabernet wine materials.

Mathematical processing of the data made it possible to reveal a close relationship between the antioxidant activity, the composition of phenolic substances and their oxidation state for white wine materials. Pairwise correlations were established between the antioxidant activity and the content of monomeric \((r = 0.90)\), oligomeric \((r = 0.92)\) and polymeric \((r = 0.98)\) forms of phenolic compounds, as well as the oxidation parameter \((r = -0.90)\). For red wine materials, a correlation between antioxidant activity and oxidation parameter of phenolic substances has not been established.
Figure 5. Mass concentration and antioxidant activity of phenolic substances in Rkatsiteli and Cabernet wine materials.

Thus, the oxidation state of phenolic substances in white table wine materials has a direct effect on their antioxidant activity. The oxidation parameter of phenolic substances, which characterizes the ability of phenolic substances to oxidize, depends on the content of the main forms of phenolic compounds and can be used as a criterion for evaluating the antioxidant properties of white table wine materials and wines [18-20]. The close relationship between the oxidation parameter of phenolic substances and the values of antioxidant activity in white wine materials indicates the possibility of using the oxidation parameter to assess the antioxidant activity in white wine materials and wines.

4. Conclusions
A correlation has been established between the antioxidant activity of white table wine materials, an indicator of the oxidizability of phenolic substances, the content of monomeric, oligomeric and
polymers of phenolic compounds. It has been shown that the oxidation state of phenolic substances in white table wine materials has a direct effect on their antioxidant activity. It has been established that the oxidation parameter of phenolic substances, which characterizes the ability of phenolic substances to oxidize, can be used as a criterion for evaluating the antioxidant properties of white table wine materials and wines. The method of potentiometric titration is recommended for evaluating the antioxidant activity of white table wine materials and wines.

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