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DETERMINATION OF TOTAL ACID CONTENT IN WINE BASED ON THE VOLTAMMETRIC REDUCTION OF 1,4-BENZOQUINONE

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ABSTRACT. In this work, voltammetric determination of the total acid content in wine was made, by measuring the reduction prepeak current of p-benzoquinone (BQ). This prepeak is due to the presence of acids in unbuffered ethanol medium. The simple system of p-benzoquinone was found to be suitable for this determination, because of its reduction potential, stability and solubility in ethanol containing organic acids. On the voltammograms of BQ, obtained in standard synthetic ethanolic solutions of organic acids, such as tartaric, citric and acetic, a well-defined single prepeak appeared during the cathodic potential scan. Its height was proportional to the total acid concentration. The values of total acid content of 5 wine samples and of a vinegar sample were determined by the present method, which is superior in sensitivity and requires a very small volume of wine sample compared to the conventional potentiometric titration method.

Keywords: voltammetry, total acid determination, wine, quinone

Introduction

In wines are present various organic acids, such as tartaric, malic, citric and acetic acid. Acid content doesn't rest unchanged in time, it changes during the fermentation of grape juice. Total acid content is expressed in terms of "total acidity" or "total acid" and serves as an indicator of wine taste and aroma. Total acid determination is essential for the control of fermentation and quality of wine.

Titration with NaOH using phenolphthalein as an indicator is the official method for total acid determination in wine [1]. But the results are not always satisfactory owing to vagueness of the indicator colour change, especially for the red and rose wines. Potentiometry is thus strongly recommended as an alternative method, in which the end point is defined as alkali consumption up to a given pH, e.g., pH 7 in the European standard method. The acidity corresponding to the alkaline consumption is called "titratable acidity". Though, pH values at the end points differ from wine to wine and so, the accuracy of the results may be affected. Thus it was needed a more sensitive, simple and rapid method to be found for the total acidity of wines determination.

S. Ohtsuki and Co. developed a new voltammetric method for determining the total acid content in wine, based on the fact that acids in

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unbuffered ethanol solutions of 3,5-di-t-butyl-1,2-benzoquinone (DBBQ) gave rise to a new peak (termed the prepeak) on a voltammogram at more positive potentials than that corresponding to the normal reduction peak of DBBQ. The total acid content of wines was determined from the prepeak height [2].

Same as wines, vinegar also contains various organic acids and acidity quality control is necessary in order to produce vinegar. Normally, the titratable acidity of vinegar is to be around 9% in Romania. Therefore, an acidity determination is essential to control the fermentation and quality of vinegar.

The same team of researchers established also a new method for the determination of titratable acidity in vinegar, based on the same principle like the determination of wines total acidity: the reduction prepeak of 3,5-di-t-butyl-1,2-benzoquinone due to the presence of acids in unbuffered solution [3].

The previous studies made by Ohtsuki et all involved a quinone with a complicated structure, and therefore not advantageous economically (expensive enough). In the present study, the total acid content determination was made by voltametry using one of the most common quinones: 1,4-benzoquinone and a classic three-electrode electrochemical cell.

Experimental

Reagents and solution preparation

Red and white wines examined were obtained from commercial sources. 1,4-Benzoquinone (BQ, 98%) was from Merck.

Ethanol (95%, Reagents SRL) solution containing 0,1 M $LiClO_4$ (98%, Fluka) was used as the supporting electrolyte. BQ solution was prepared by dissolving an appropriate amount of BQ (98%, Merck) in the supporting electrolyte to a concentration of 3×10^{-3} M. Test solutions were made by adding 500 µL of wine to the BQ solution (40 mL).

Reagent grade tartric acid, citric acid (anhydrous, >98 %) and acetic acid (99, 8%, Primexchim) were used to prepare standard acid solutions by diluting with the BQ solution.

Apparatus

Voltammetric measurements were made using a potentiostat-galvanostat system – BAS 100B (Bioanalytical Systems, USA) with the specific software BAS 100W and a classic three-electrode electrochemical cell. The electrochemical cell is comprised of a cell bottom of 20 mL capacity and a plastic cell top. A working electrode of vitreous carbon (2 mm diameter), an Ag/AgCl reference electrode and a platinum plate auxiliary electrode were inserted through the cell top into the cell. The pH measurements for the wines were made with a pH-meter Basic 20 from Crison.

Procedure

Cyclic voltammetry and linear sweep potential voltammetry were performed in the usual way with a potential sweep rate of 5 mV/s at 25º C. The sensitivity is 10 μA/V and the domain of potential was established after several determinations: -400 to 400 mV vs. Ag/AgCl. During the voltammetry determination, a salt bridge for the protection of the reference electrode Ag/AgCl was used.

RESULTS AND DISCUSSIONS

Choice of quinone reagent

In the study of Ohtsuki [2] a substituted quinone has been used, 3, 5-di-t-butyl-1, 2-benzoquinone (DBBQ). This quinone gave a well-defined reduction prepeak and it proved a good stability in ethanol solution in time, but we supposed that the simple benzoquinones can be used too. We choose the 1, 4-benzoquinone, one of the most simple quinone systems, for the present study, for economical reasons for the study of a cheaper way to apply this method of total acid content determination.

To avoid overlap of the prepeak and the reduction peak of dissolved oxygen in the solution, use of quinones reduced at potentials more positive than -0,4 V (vs. Ag/AgCl) is desirable. p-Benzoquinone reduces at a potential more positive than -0,4 V vs. Ag/AgCl, so that dissolved oxygen causes no interference in measuring the prepeak height. The stability of BQ in ethanol was demonstrated by time-course measurements of absorption UV-Vis spectrum (λ_1 = 244 nm, log ϵ_1 = 4.3; λ_2 = 279 nm, log ϵ_2 = 2.8; λ_3 = 430 nm, log ϵ_3 = 1.3).

Acid determination in synthetic solutions, based on the voltammetric reduction of BQ

Following the addition of tartaric acid into the BQ solution, a prepeak appeared at a potential more positive than that corresponding to the original reduction peak, as shown in figure 1 and 2. The preapeak of benzoquinone reduction in presence of tartaric acid occurs at 0.1 V vs. Ag/AgCl.

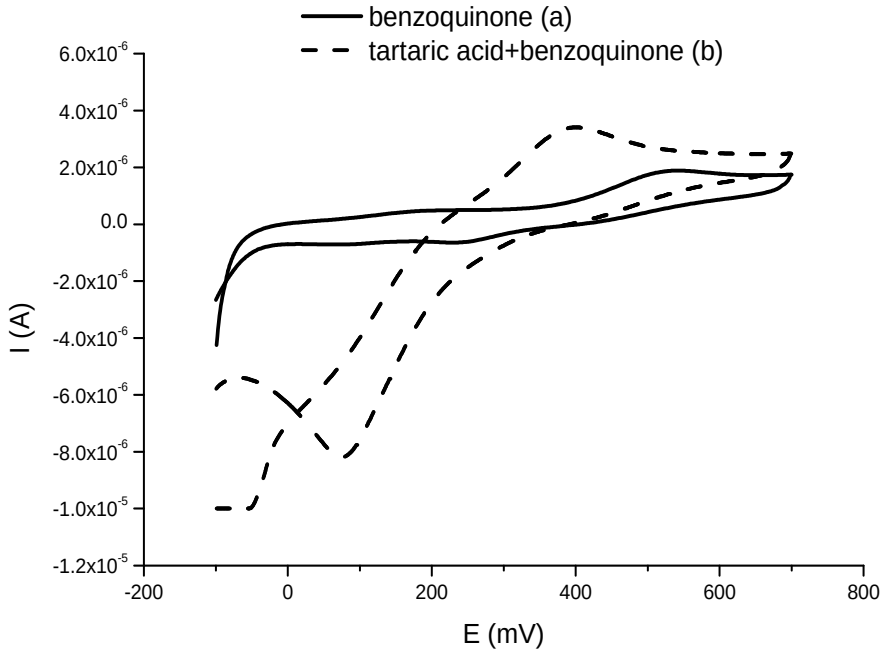

Fig.1. Cyclic voltammograms of $3x10^{-3}$ M 1,4-benzoquinone in absence (a) and in presence (b) of $1,2x10^{-3}$ tartaric acid in ethanol containing 0,1 M $LiClO_4$. WE: VC, RE: Ag/AgCl, CE: platinum plate; scan rate: 5mV/s

The prepeak height was found to be proportional to the tartaric acid concentration from $5x10^{-4}$ M to $1.5x10^{-2}$ M with a correlation coefficient of 0,996. The relative standard deviation (RSD) of the prepeak height obtained with $5x10^{-4}$ M tartaric acid was 2% (n = 5).

Electrochemical reduction of quinone in amphiprotic solvents is known to involve a two-electron transfer coupled with a two-proton transfer to form the corresponding hydroquinone. In previous studies of proton donor effects on the voltammetric reduction of quinone in an unbuffered solution [2], the prepeak current was found to be controlled by the diffusion of the acid in the electrolyte solution to the electrode surface.

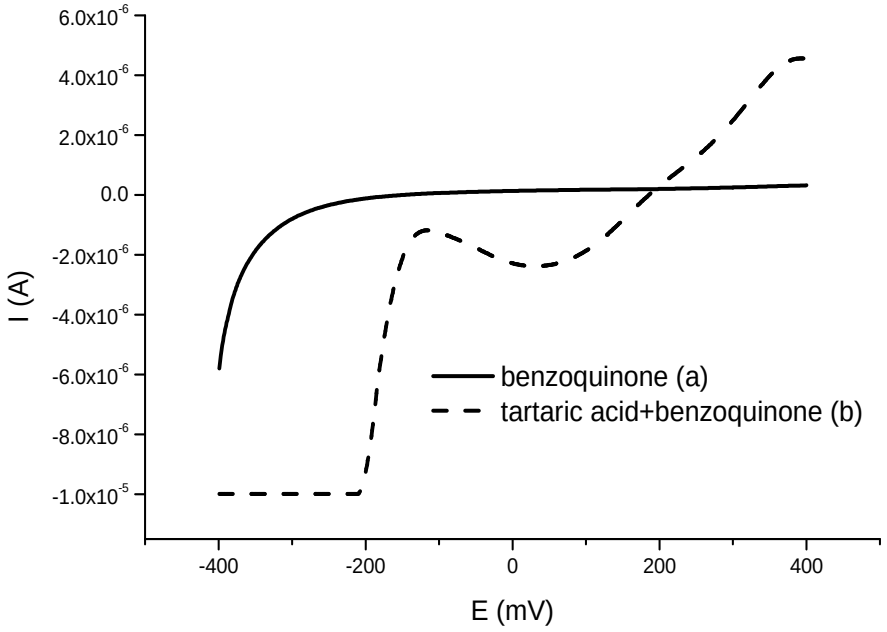

Fig.2. Linear sweep voltammograms of $3x10^{-3}$ M 1, 4-benzoquinone in absence (a) and in presence (b) of $1.2x10^{-3}$ tartaric acid in ethanol containing 0.1 M $LiClO_4$. WE: VC, RE: Ag/AgCl, CE: platinum plate; scan rate: 5mV/s

The electrolysis of quinone at the prepeak potential demonstrated that hydroquinone was likewise produced through a two-electron reduction process, although the electrolysis potential was more positive than the normal reduction potential [4]. Based on this fact, the occurrence of the prepeak can be ascribed in the increased availability of protons from the added acid compared to solvent molecules. This results in a lowering of the free energy for the reduction process, leading to a reduction potential shift in the positive direction depending on the acid strength [4 – 6].

Addition of various carboxylic acids to individual BQ ethanol solutions gave rise to a single prepeak at -0.22 to 0.05 V (vs. Ag/AgCl), as shown in figure 3 and 4. In all cases, each acid concentration was the same, but the prepeak height differed according to the number of protons available for the transfer. For the citric acid, the preapeak occurs at -0.2 V vs. Ag/AgCl and for the acetic acid, the reduction prepeak occurs at 0.05 V vs. Ag/AgCl. The prepeak of BQ in presence of acetic acid is less visible,

probably due to the more reduced electrosorbtion of acetic acid at the surface of the electrode, compared to the tartaric and citric acid.

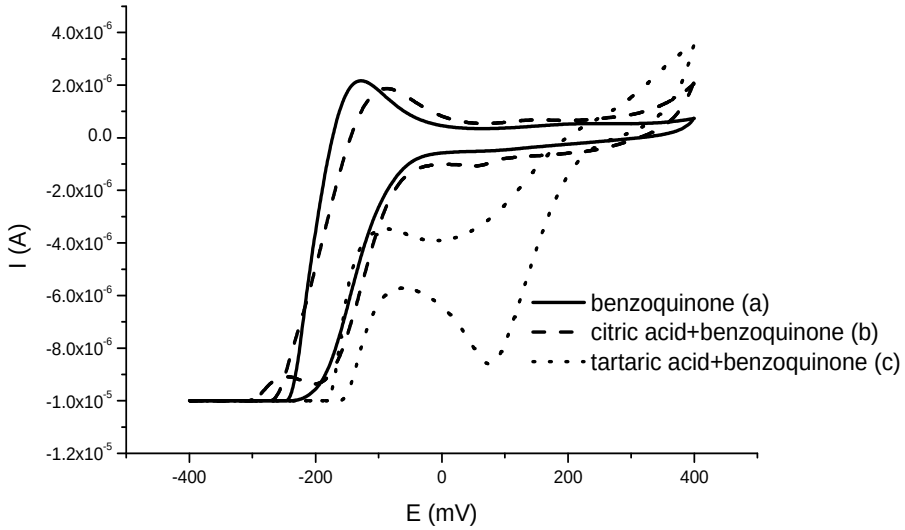

Fig.3. Cyclic voltammograms of $3x10^{-3}$ M 1,4-benzoquinone in absence (a) and presence of $1,2x10^{-3}$ citric acid (b) and $1,2x10^{-3}$ tartaric acid (c) in ethanol containing 0.1 M $LiClO_4$. WE: VC, RE: Ag/AgCl, CE: platinum plate; scan rate: 5mV/s

The prepeak height was found to be linearly related to the equivalent concentration for the acetic acid ranging from $5x10^{-5}$ M to $2,5x10^{-3}$ M, with a correlation coefficient of 0,998. The equation of the calibration curve for tartaric acid is: y = -3,7107x – 0,571. The relative standard deviation (RSD) of the prepeak height obtained with $5x10^{-4}$ M acetic acid was 1,6% (n = 5).

The occurrence of a prepeak current in the case of benzoquinone reduction in an unbuffered medium in presence of an organic acid does not depend on the nature of the acid. Though, the nature of the acid can influence the position and the prepeak form. The preapeak current has a linear variation with the acid's concentration for a domain of concentrations large enough. These concentrations are to be found within the limits of the acid's usual concentrations in wines. In this case, the calibration curve found for the tartaric acid can be used successfully for determining the acidity of real wine samples. The calibration curve for the acetic acid can be also successfully used for determining the acidity of vinegar.

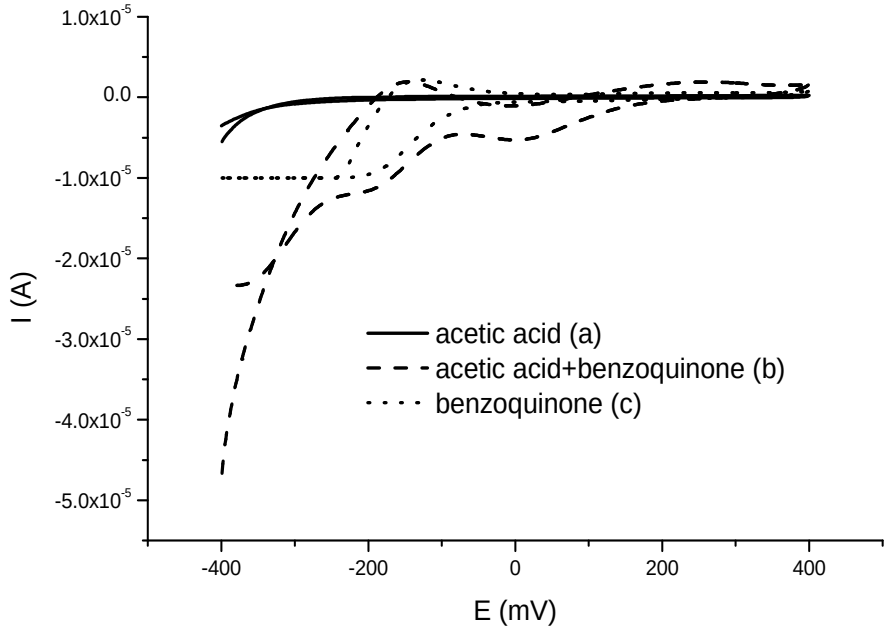

Fig.4. Cyclic voltammograms of $1.2x10^{-3}$ acetic acid in absence (a) and in presence of $3x10^{-3}$ M 1,4-benzoquinone (b) in ethanol containing 0.1 M $LiClO_4$. WE: VC, RE: Ag/AgCl, CE: platinum plate; scan rate: 5mV/s

Total acid determination of wine

Various acids contained in wine gave rise to a prepeak on the voltammogram of BQ. By the addition of 500 µL of wine to 40 mL of the BQ solution, a prepeak occurred. The total acid content in wine is calculated, based on the calibration curve obtained for the tartaric acid. The total acid content should be converted to the concentration of tartaric acid (g/10 mL), according to the definition of the total acidity of wine in the official analytical methods.

The present method was applied to the total acid determination of 5 different kinds of wines, and the results are listed in table 1. For each kind of wine 5 determination were performed and the RSD is for all of them under 2%. For comparison pH measurement is showed also (table 1). However, total acid content may not always be closely related with pH values, since the latter reflects the hydrogen ion activity in the acid mixture solution.

Table 1.

Total acid content in wine, as tartaric acid

Wine	pH	Total acid content ($x10^{-2}$ g/10 mL)
Red, Pinot Noir, 2006	3,35	5,78
Red, Pinot Noir, 2003	3,55	5,53
Red, Feteasca Neagra, 1999	3,30	6,22
White, Chardonnay Koşer Pesah, 2003	3,18	6,19
White, Aiud producer, 2006	3,25	7,09

The concentration of acetic acid in 9% vinegar was also verified, based on the calibration curve of acetic acid. The concentration value for the acetic acid found by voltammetric determination is 9,08%, value very close to the real one (known). The relative standard deviation (RSD) of the prepeak height obtained was 1,62% (n = 5).

CONCLUSIONS

The present method was shown to be practically useful for determining the total acid content in wine and vinegar. The method is straight forward and simple to use. Dissolved oxygen in the test solution has no effect on the measurement of the prepeak height, leading to a considerable reduction of the operation time. Also, sample colour and turbidity cause no interference on the analytical results. This methods is sensitive and accurate, it requires small sample volumes (500 µL) and the RSD values are less than 2 %. Determination of total acid content of wines and vinegar by electrochemical reduction of quinones has the advantage of the electrochemical methods – rapidity, sensitivity, precision and not last – it is an environmental friendly method.

As perspectives, it is envisaged to use this method as a suitable alternative for titratable acidity determination, not only in wine and vinegar, but also in food, fruit, alcoholic and non-alcoholic beverages.

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