Comparative Study of the Total Acidity Determination in Wine by Potentiometric and Volumetric Titration

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Summary

Total acidity was determined in thirty-seven samples of Croatian red, white and rosé wines by potentiometric titration. In order to find the effect of the corresponding rate of the automatic titrant added, several procedures were employed. For different rates of titration, the aberrances were found from 0.1 to 0.4 g L^{-1} for some wines. The value of the total acid content in wine determined by the automatic potentiometric titration method was compared to that obtained by the conventional volumetric titration method. The ANOVA and cluster analysis (CA) were applied to detect possible resemblance. The results of total acidity depended on the methods used. However, a good correlation between the results by these methods was found.

Key words

wine; total acidity; potentiometric titration; volumetric titration

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Introduction

Titration is a widely used technique to monitor many processes. However the long time required presents disadvantage when a manual titrimetic procedure is employed. To overcome this drawback, automatic batch titrators and continuous flow techniques have been proposed (Martelli et al., 1999).

Wine contains the acids of must and a number of acids produced during and after alcoholic fermentation. Acids play a key role in keeping the wine microbiologically and chemically stable. In addition, they have a large effect on the colour, taste and stability of the final product. Two acid-related parameters of interest in monitoring wine production are the total and volatile acid. The former is defined as sum of titratable acids when the sample is neutralized at pH 7.0. The parameter is also known as titration acidity.

Total wine acidity is one of the most important factors in determination of its quality in wine cellars during winemaking and ageing (De Castro et al., 2005). The analysis of total acidity allows us to control the process of alcoholic fermentation, malolactic fermentation, aging, etc. (Peynaud, 1999). Total acidity is used during processing and finishing operations to standardize the wines and to follow undesirable changes due to bacteria, yeasts, etc. (Ough and Amerine, 1988).

The official O.I.V. (Office International de la Vigne et du Vin) analysis method for determination of total acidity in wine is titration with NaOH using bromothymol blue (6.0< pH< 7.6 yellow-blue transition) as an indicator which changes colour at pH=7 (EU, 1990). However, in some cases acid-base titrations such as titration of dark-coloured red wines or rosé wines are difficult to accomplish using a visual indicator due to a particular indicator colour change. In such situations, potentiometric titration, using a glass hydronium ion selective electrode, a suitable reference electrode or combined pH glass electrode and a sensitive potentiometer might be advantageous. Additionally, the analytical results might be different depending on the determination procedure (Diaz et al., 2003.) Although there are some literature data (Lucan and Palic, 1994; Rudan-Tasic and Klofutar, 1998) about total wine acidity, data about the total wine acidity measured by automatic potentiometric titration using different rates of adding titrating reagents have not been found. Therefore, the aim of our research is to determine the influence of different rates of automatic potentiometric titration on the total acidity of Croatian wines and to find a connection between the results of potentiometric and volumetric titration measurements to confirm the influence of used methods on the quality assessment.

Materials and methods

Wine samples

Thirty-seven commercial wines (18 white, 18 red and one rosé) were investigated in this study. These wines were produced in Dalmatia, the coastal region of Croatia and were obtained from the market. Of the 37 samples of commercial wines, 13 were table wines, 22 were quality wines, and two were wines of high quality (see Table 1).

Reagents

Buffer solutions with pH = 4.00 and pH =7.00 were used for calibration of the Methrom potentiometer. Titrations were performed using a sodium hydroxide solutions, c (NaOH) = 0.1000 mol L^{-1}. Buffer solutions were from Merck (Germany). Sodium hydroxide solution was from Kemika (Zagreb, Croatia).

Potentiometric apparatus and procedure

The potentiometric measurements were performed at T = (20±0.1) °C with a Methrom potentiometer (Titrino), model 702 SET/MET, equipped with a combined pH glass electrode with temperature sensor and a magnetic stirrer. The titrant was dispensed with a Dosimat burette, model 765 by Methrom (accuracy ±0.01 cm^3). The titrant was 0.1 mol L^{-1} NaOH solution. The glass electrode was calibrated in - log[H^+] units (pH) with IUPAC standard buffers of pH=4 and pH=7.

10 mL of the wine sample were diluted with 10 mL of distilled water in a glass beaker. After calibration, glass electrode was immersed in the wine sample. The sample was titrated with the c(NaOH) = 0.1000 mol L^{-1} to pH = 7 using the automatic SET mode. During the titration the sample was stirred using a magnetic stirrer. Each measurement was performed with three parallel determinations. The results are given in g L^{-1} tartaric acid as average values of three measurements.

Volumetric titration

The method is based on the titrations of free forms of acids in wines with c(NaOH) = 0.1000 mol L^{-1} in the presence of bromothymol blue as an indicator.

Statistical analysis

Results for acidity of white and red wines (there was only one sample of rosé wine) at different rates of titrant addition and the results of volumetric method were tested by ANOVA as well as using cluster analysis (CA) with the Statistica 7.0 package (StatSoft, Inc., Tulsa, OK, USA). Separate analyses for samples of white and red wines were done.

Results and discussion

Potentiometric titration

Total acidity of 37 wine samples was measured by potentiometric titration using automatic potentiometric titrator. All measurements were done at 20 °C to avoid the influence of temperature on the rate of chemical reaction. End point of potentiometric titration was determined with glass electrode at pH = 7.

According to the OIV procedure, end point of equivalence was reached at pH value of 7 (EU, 1990). From the electrode potential change a volume of equivalence of acid-base reaction was detected, where the change in the activity of H^+ was done.

Results of pH determination in all wine samples are shown in Table 1. It was noticed that the range of pH values was between 2.75 and 3.4, which is in agreement with literature data (Lucan and Palic, 1994; Ribéreau-Gayon et al., 2000).

It was noticed that white table wines (2.75-3.04) as well as red table wines (3.03-3.18) had lower pH values then quality white wines (2.87-3.34) and quality red wines (2.86-3.22).

Table 1. Results of pH value of wines

Sample	Wines	Type	Year	Quality	pH
1	Vugava	white	2003	highest quality	3.33
2	Žilavka	white	2003	quality	2.98
3	Debit	white	2001	quality	3.14
4	Maraština	white	2001	quality	3.09
5	Debit	white	2003	quality	3.22
6	Maraština	white	2003	quality	3.34
7	Malvazija	white	2002	quality	3.03
8	Debit	white	2003	quality	3.00
9	Medna	white	2000	quality	3.00
10	Kaštelet	white	2002	quality	2.87
11	Table wine	white	2003	table	2.96
12	Table wine	white	2003	table	3.04
13	Table wine	white	2003	table	3.00
14	Table wine	white	2003	table	2.93
15	Table wine	white	2003	table	3.18
16	Table wine	white	2003	table	2.79
17	Table wine	white	2003	table	3.03
18	Table wine	white	2003	table	2.75
19	Babić	red	2003	highest quality	3.46
20	Babić	red	2003	quality	3.16
21	Dalmatiner rot	red	2003	quality	3.03
22	Dalmatinska kapljica	red	2002	quality	3.06
23	Plavac Marjan	red	2002	quality	3.07
24	Plavac Marjan	red	2003	quality	3.00
25	Plavina	red	2001	quality	2.86
26	Plavina	red	2003	quality	3.22
27	Lasina	red	2001	quality	2.87
28	Lasina	red	2003	quality	3.21
29	Pelješac	red	2003	quality	3.17
30	Kaštelet	red	2002	quality	3.05
31	Kaštelet	red	2003	quality	2.99
32	Table wine	red	2003	table	3.18
33	Table wine	red	2003	table	3.07
34	Table wine	red	2003	table	3.12
35	Table wine	red	2003	table	3.13
36	Table wine	red	2003	table	3.03
37	Vrgorački Rosé	rosé	2003	quality	3.06

Wines with pH = 3.4 or lower were more resistant to bacteria and microbiological spoilage, in comparison with wines with higher pH (Ough and Amerine 1988; Jackson 1994; Ribéreau-Gayon et al., 2000).

Díaz et al. (2003) also found lower pH values for white (3.11) and rosé (3.19) wines than for red ones (3.55).

Table 2 shows the results of total acidity of 37 different Croatian wines measured by automatic potentiometric titration with different rates of addition of titration reagents and as well as total acidity determined by volumetric titration. Total acidity was determined with titration process using a standard solution of NaOH with rates of adding the titration reagent of 2, 4, 6, 8 and 10 mL min^{-1} with intention to define the influence of different titration rates on results of measurement. Based on the experimental results shown in Table 2 it was perceived that decreasing the titration rates from 10 to 2 mL min^{-1} resulted in lower total acidity of all wines.

The difference in total acidity was between 0.1 and 0.4 g L^{-1}. The highest total acidity was detected with titration rate of 10 mL min^{-1} and it had the value of 7.03 g L^{-1} (Plavina, sample 25), while the mean total acidity (for different rates) for this sample was 6.80 g L^{-1}. Furthermore, in this wine total acidity of 6.60 g L^{-1} was measured with the rate of 2 mL min^{-1},

These differences could be due to the response of the pH electrode that occurred during faster or slower movement of acid-base equilibrium reaction towards to the reaction product. The lowest total acidity of 4.12 g L^{-1} (wine Debit, sample 5) was measured at the rate of 2 mL min^{-1}, while the acidity value of the same sample at the rate of 10 mL min^{-1} was 4.47 g L^{-1}, and the mean value of the acidity was 4.26 g L^{-1}.

Comparison of total acidity measured by potentiometric and volumetric titration

The results of total acidity measured by potentiometric titration were compared with the results measured by volumetric titration in order to detect the influence of the method on the results. The comparison of the results of potentiometric and volumetric titration for white and red wines are presented in the Figures 1 and 2. The difference in the results for total acidity was observed in relation to titration rate. For the wine Žilavka and for the table wine (samples 2 and 15), no difference in total acidity between those two methods of titration was found at the average titration rate of 6 mL min^{-1}, while the highest difference between those two methods was 0.29 g L^{-1}. The highest total acidity measured by potentiometric titration was 7.03 at the rate of 10 mL min^{-1}, and 6.81 g L^{-1} at the average rate of 6 mL min^{-1}, while the acidity measured by volumetric titration was 6.52 g L^{-1}.

The values for acidity of white and red wines at different titration rates were compared with the results of volumetric method and tested using t-test as well as multi-variant analysis. The differences for all rates of adding titrant were detected.

From the results presented in Fig.1, the results of measurements at average titration rate of 2 and 4 mL min^{-1} seem to be the most similar to the volumetric measurements. To confirm this idea, the Cluster Analysis was conducted.

As presented in the dendrogram in Fig. 2, the highest difference from the volumetric method was found at titration rate of 10 mL min^{-1}, while the best correspondence between volumetric measurements and titrations at different rates of adding titrant was found at the rate of 2 and 4 mL min^{-1}. In order to determine which one of these two titrations showed better correspondence to volumetric measurements, t-test was used and p-values were calculated. The results of the rate of adding titrant of 2 and 4 mL min^{-1} were compared with volumetric measurements and the p-value for white and red wines at 2 (p_{white}=0.991215; p_{red}=0.99614) was higher than that computed at 4 mL min^{-1} (p_{white}=0.842082; p_{red}=0.62114). This fact indicates that the similarity of white and red wines measured at the rate of 2 mL min^{-1} is more similar to volumetric method data then at the rate of 4 mL min^{-1}. However, in some wine samples (white wine no. 1, and red wines no. 26, 27 and 35) the considerable aberration has been found.

In general, the results of total acidity in this research were slightly lower than those published earlier (Lucan and Palic 1994; Rudan-Tasic and Klofutar 1998), but the main differ-

Table 2. Total acidity (g L^{-1}) determined at different rate of automatic potentiometric titration and total acidity determined by volumetric titration

Sample	Potentiometric titration - Titration rate (ml min $^{-1}$)					Volumetric titration
	10	8	6	4	2	
1	4.68 ± 0.03	4.62 ± 0.02	4.56 ± 0.01	4.41 ±0.01	4.39 ± 0.01	4.63 ± 0.01
2	5.30 ± 0.06	5.27 ± 0.03	5.26 ± 0.04	5.21 ±0.03	5.20 ± 0.02	5.19 ± 0.02
3	5.77 ± 0.03	5.74 ± 0.05	5.68 ± 0.08	5.62 ± 0.07	5.47 ± 0.02	5.39 ± 0.02
4	5.25 ± 0.12	5.18 ± 0.01	5.16 ± 0.05	5.00 ± 0.01	4.81 ± 0.01	-
5	4.47 ± 0.24	4.40 ± 0.01	4.17 ± 0.04	4.15 ± 0.01	4.12 ± 0.06	-
6	4.53 ± 0.05	4.39 ± 0.04	4.33 ± 0.04	4.26 ± 0.04	4.20 ± 0.04	4.09 ± 0.02
7	6.88 ± 0.01	6.80 ± 0.14	6.75 ± 0.03	6.62 ± 0.08	6.58 ± 0.06	6.70 ± 0.02
8	5.69 ± 0.08	5.57 ± 0.04	5.50 ± 0.04	5.46 ± 0.08	5.39 ± 0.03	3.37 ± 0.02
9	5.32 ± 0.01	5.21 ± 0.01	5.14 ± 0.02	5.11 ± 0.01	5.05 ± 0.03	-
10	5.84 ± 0.01	5.79 ± 0.03	5.73 ± 0.02	5.68 ± 0.01	5.58 ± 0.02	5.58 ± 0.03
11	5.30 ± 0.06	5.26 ± 0.02	5.24 ± 0.04	5.20 ± 0.02	5.19 ± 0.01	-
12	5.66 ± 0.02	5.63 ± 0.06	5.43 ± 0.03	5.42 ± 0.03	5.35 ± 0.06	5.29 ± 0.01
13	5.21 ± 0.02	5.19 ± 0.01	5.09 ± 0.02	4.99 ± 0.01	4.91 ± 0.02	4.89 ± 0.02
15	4.89 ± 0.01	4.69 ± 0.02	4.66 ± 0.04	4.54 ± 0.01	4.55 ± 0.03	4.62 ± 0.02
16	5.95 ± 0.07	5.84 ± 0.04	5.72 ± 0.10	5.64 ± 0.01	5.62 ± 0.01	5.51 ± 0.01
17	5.99 ± 0.04	5.94 ± 0.01	5.90 ± 0.01	5.88 ± 0.01	5.87 ± 0.01	-
18	5.47 ± 0.02	5.39 ± 0.02	5.33 ± 0.01	5.31 ± 0.01	5.25 ± 0.01	5.25 ± 0.04
19	6.61 ± 0.18	6.48 ± 0.04	6.46 ± 0.01	6.46 ± 0.04	6.45 ± 0.04	-
20	5.90 ± 0.07	5.87 ± 0.10	5.80 ± 0.02	5.73 ± 0.04	5.70 ± 0.01	5.52 ± 0.02
21	5.70 ± 0.17	5.54 ± 0.03	5.51 ± 0.80	5.37 ± 0.03	5.34 ± 0.03	-
22	5.37 ± 0.01	5.34 ± 0.03	5.20 ± 0.03	5.14 ± 0.02	5.07 ± 0.06	-
23	5.52 ± 0.02	5.39 ± 0.04	5.32 ± 0.03	5.23 ± 0.04	5.18 ± 0.01	5.19 ± 0.01
24	5.40 ± 0.02	5.33 ± 0.03	5.28 ± 0.06	5.19 ± 0.01	5.09 ± 0.03	5.06 ± 0.06
25	7.03 ± 0.07	6.89 ± 0.01	6.84 ± 0.05	6.71 ± 0.04	6.60 ± 0.03	5.19 ± 0.02
26	5.52 ± 0.13	5.38 ± 0.05	5.33 ± 0.01	5.28 ± 0.04	5.21 ± 0.03	6.51 ± 0.02
27	6.40 ± 0.06	6.35 ± 0.01	6.20 ± 0.01	6.18 ± 0.01	6.13 ± 0.04	6.19 ± 0.02
28	5.75 ± 0.08	5.62 ± 0.04	5.50 ± 0.05	5.43 ± 0.03	5.41 ± 0.01	5.29 ± 0.02
29	5.30 ± 0.01	5.27 ± 0.01	5.22 ± 0.02	5.17 ± 0.01	5.15 ± 0.01	5.24 ± 0.02
30	5.61 ± 0.08	5.38 ± 0.04	5.31 ± 0.02	5.20 ± 0.01	5.18 ± 0.01	5.30 ± 0.02
31	5.40 ± 0.04	5.36 ± 0.02	5.34 ± 0.01	5.27 ± 0.08	5.19 ± 0.02	-
32	5.67 ± 0.01	5.62 ± 0.04	5.56 ± 0.01	5.50 ± 0.02	5.39 ± 0.01	5.19 ± 0.02
33	5.60 ± 0.04	5.43 ± 0.01	5.38 ± 0.01	5.36 ± 0.04	5.26 ± 0.01	5.18 ± 0.02
34	4.80 ± 0.01	4.78 ± 0.06	4.62 ± 0.06	4.55 ± 0.01	4.46 ± 0.01	4.36 ± 0.03
35	5.90 ± 0.03	5.74 ± 0.01	5.68 ± 0.01	5.63 ± 0.01	5.57 ± 0.05	5.03 ± 0.04
36	5.55 ± 0.03	5.44 ± 0.04	5.37 ± 0.03	5.35 ± 0.05	5.32 ± 0.03	5.52 ± 0.20
37	6.74 ± 0.06	6.71 ± 0.02	6.66 ± 0.05	6.59 ± 0.01	6.51 ± 0.03	5.36 ± 0.22

Values are means of three replications ± standard deviation.

ence is that the wines analyzed in this study were produced in warm climate area, near the Adriatic Sea, in the Republic of Croatia. In general, white wines had higher total acidity than

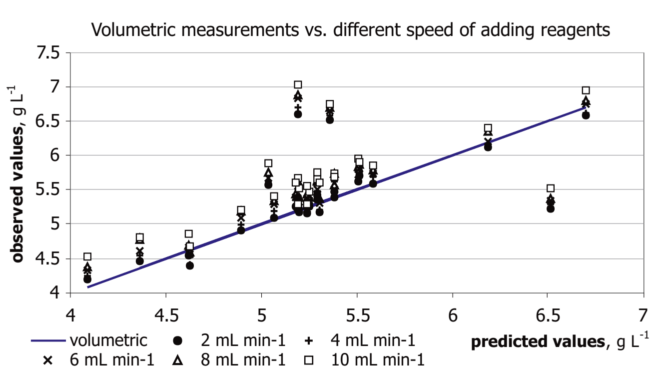

Figure 1. Comparison of different speed of adding reagents during volumetric measurements

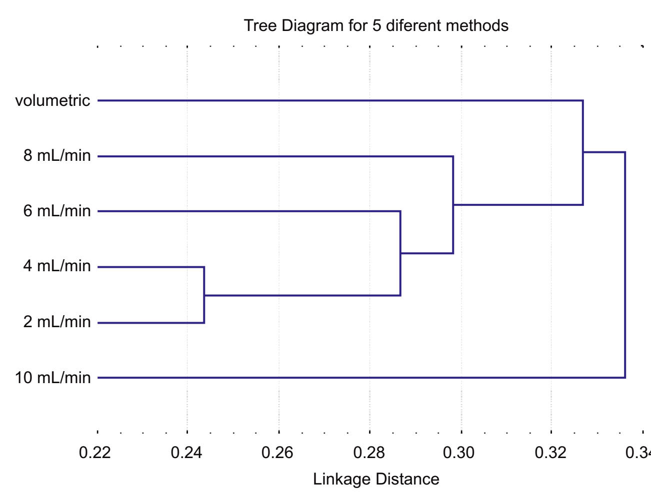

Figure 2. Dendogram based on differences between volumetric and potentiometric method at different rates

red wines, which was also in positive relation with earlier results of the comparison of these types of wine (Darias-Martin et al., 2003). The exception was red wine Plavina (sample 25) with the highest acidity of all measured wine samples.

Conclusions

An attribute of wine quality is total acidity, and it is very important to have a simple and applicable method for it detection. The aberrance in total acidity between potentiometric and volumetric titration was defined, as well as the influence of titration rate on the results. Both methods showed similar results for white and red wines. Both methods can be used for detecting of total acidity in different wines, but if the potentiometric titration method is used, the addition of the titrant should be 2 mL min^{-1} in order to obtain results of total acidity as it would be accomplished using the volumetric titration method.

The main advantage of the potentiometric method is the time saving, objectivity and precision of the method, as well as the minimization of possible sample contamination, because the sample is closed during the measurement.

References

De Castro M. D. L., J. Gonzalez-Rodriguez and P. Perez-Juan (2005). Analytical methods in wineries: Is it time to change? Food Reviews International 21: 231-265.

Díaz C., J. E. Conde, C. Claverie, E. Díaz and J. P. Pérez Trujillo (2003). Conventional enological parameters of bottled wines from the Canary Islands. Journal of Food Composition and Analysis 16: 49-56.

Darias-Martín J., A. Socas-Hernández, C. Díaz-Romero and E. Díaz-Díaz (2003). Comparative study of methods for determination of total acidity in wine. Journal of Food Composition and Analysis 16: 555-562.

European Union, (1990). Commission Regulation (EEC) No 2676/90 Official Journal of European Communities L 272/1990. Analytical methods for wine analysis.

Jackson R.S. (1994). Wine science, Principles and Applications, Academic Press. Inc. San Diego.

Lucan Z.D. and A. Palic, (1994). Total acids determination in wine with different methods. Die Nahrung 38: 427-433.

Martelli P.B., B. F. Reis, M. Korn, J. L. F. Costa Lima (1999). Automatic potentiometric titration in monosegmented flow system exploiting binary search. Analytica Chimica Acta, 387: 165–173

Ough C.S. and Amerine M.A. (1988). Acidity and Individual acids. In Methods for Analysis of Musts and Wine 2nd ed. pp 50-70. John Wiley & Sons, New York.

Ribereau-Gayon P., Y. Glories, A. Maujean and D. Dubourdieu (2000). Handbook of enology, vol. 2. The chemistry of wine stabilization and treatments, Wiley, New York.

Rudan-Tasic D. and C. Klofutar (1998). Gran's plots for end point detection in potentiometric titration of wine. Analysis 26: 25-28.

Takamura K., S. Ohtsuki and F. Kusu (2001). Development of new amperometric sensor for probing the total acid of beverages. Analytical Sciences 17: 737-I 739.

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