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Gran's plots for end point detection in potentiometric titration of wine*

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Abstract. In several samples of Slovenian white wine the concentration of ethanol in extract, pH values, and total acidity were determined, as well as the densities and refractive indices. Total acidity was determined by a classical procedure which is the accepted method of the *American Society of Enologists* and the *AOAC*, i.e. the titration of wine with a strong base up to the titration "end point" at pH 8.2. In order to find the true end point, *Gran's* graphical procedure was employed and some examples of its practical application are illustrated. A *Gran's* plot converts a logarithmic response to a linear plot and it is shown that in spite of the complex wine matrix, this analytical procedure enables a precise, reproducible and accurate determination of the total acidity of wine.

Key words. Wine – total acidity – potentiometric titration – graphical procedure.

Introduction

The acid content of a wine is of importance from the standpoint of flavour and, indirectly, by its effects on pH, colour, stability, and shelflife of the product. The acid levels are influenced by variety, climatic conditions, cultural practices, and the maturity of the grapes. The total (titratable) acidity is used during processing and finishing operations to standardize wines and to follow undesirable changes due to bacteria, yeasts, etc. The acids present in wines (tartaric, malic, citric, acetic, succinic, and lactic are common) are relatively weak organic acids. Thus when musts or wines are titrated with a strong base, the true end point will be greater than 7.0 on account of hydrolysis of the salts. Moreover, the total acidity, determined by potentiometric titration to the agreed-on end point of pH 8.2 [1,2] seems to be low as well. Above all, the pH value at the end point, pH_e, cannot be exactly of a unique value for all wines; it changes with acid composition and concentration [3]. The purpose of this study was to find out a precise, reproducible and quick method for determination of the total acidity of wine and to show the discrepancy between the real pH_e and the normative value of 8.2 or even 7.0.

Experimental

Sample preparation for analysis

Twenty samples of *Slovenian* wine (samples 1 to 8 were white and dry, samples 9 to 20 were white and medium dry, see Tabs. I and II) were just filtered (for density and refractive index measurements) or they were filtered and then CO_2 was removed (for potentiometric analysis) by rapid heating of the sample up to the boiling point (half a minute). After the gas has been removed the sample was cooled quickly to 298 K.

Density measurements

Density measurements were carried out using an *A. Paar* digital densimeter (model DMA 100) at a temperature of 298.15 ± 0.02 K. The densimeter was calibrated with water [4] and dry air [5]. The ethanol and extract content was determined by procedures given in the literature [6] and [7].

Refractive index measurements

Refractive indices were measured at 298.15 ± 0.05K with a *Carl Zeiss Abbé* refractometer (32-G 110e) with a precision of $1 \cdot 10^{-4}$ at a wavelength of 589 nm.

pH measurements

pH values of the wines themselves, as well as changes during potentiometric titration were recorded using a pH-meter (*Radiometer*, type PHM250 Ion Analyzer) with a glass combined electrode (*Radiometer*, type C2401-8). The pH-meter was standardized with four IUPAC standard buffers (pH range from 3 to 10, [8]).

Potentiometric titration

Potentiometric titrations of wine samples with a standard solution of sodium hydroxide (c = 0.1 mol dm^{-3}) were performed in three parallel determinations in a titration vessel at 298.15 ± 0.05 K by means of a digital burette (accuracy ± 0.01 cm^3). To reduce the concentration of ethanol and accordingly its influence on solvent and solute properties (e.g. changes in their activity coefficients), an aliquot of 5 cm^3 of wine sample was diluted with 100 cm^3 of boiled (and cooled) deionized water for each potentiometric titration.

Results and discussion

Several methods can be used to determine the end point of a potentiometric titration. One problem with using

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derivatives [9] to find the end point is that titration data are most difficult to obtain close to the end point, because buffering is minimal and electrode response is sluggish. A *Gran* plot [10,11] is a graphical method that allows us the use of data from before (or after) the end point to localize the end point. Moreover, the titration curve need not be symmetric about the equivalence point.

A volume V of acid is titrated with a volume v of a strong base of concentration B in the galvanic cell the electromotive force of which is determined by means of a pH-meter;

$$(-)\ \begin{matrix}\text{electrode reversible to}\\ \text{hydrogen ions}\end{matrix}\ \Big|\ \begin{matrix}\text{titration}\\ \text{solution}\end{matrix}\ \Big\|\ \begin{matrix}\text{reference}\\ \text{half - cell}\end{matrix}\ (+) \qquad (1)$$

such a potential difference is given by

$$E = E_o' - \frac{RT}{F} \ln \left[H^+\right] \gamma_{H^+} + E_j \qquad (2)$$

where E_o' includes the potential of the reversible and reference electrode, E_j is the liquid junction potential, R is the gas constant, F the *Faraday* constant, T the absolute temperature, $[H^+]$ the molarity of free hydrogen ions and γ_{H^+} the activity coefficient of hydrogen ions.

Because wine is a complex mixture of several weak acids, both mono and polyprotic ones, we used *Gran's* graphical method of end point determination for the alkaline range, i.e. after the equivalence point, v_e. In this range, $v \geq v_e$ and the concentration of hydrogen ions is given by the relation

$$\left[H^+\right] = \frac{K_w}{\left[OH^-\right]} = \frac{K_w\left(V+v\right)}{B\left(v-v_e\right)} \qquad (3)$$

where K_w is the ionic product of water. Taking into account the relation for the activity of hydrogen ions, $a_{H^+} = [H^+]\ \gamma_{H^+} = 10^{-pH}$ in equation (3) it follows

$$\left[H^+\right] = \frac{10^{-pH}}{\gamma_{H^+}} = \frac{K_w\left(V+v\right)}{B\left(v-v_e\right)} \qquad (4)$$

If pH is measured directly, we may make use of a function defined as

$$\Phi' = \frac{B\left(v-v_e\right)}{K_w\,\gamma_{H^+}} = \left(V+v\right)\ 10^{pH} \qquad (5)$$

Instead of pH the potential E can be determined and, taking into account relations (2) and (3), it follows

$$\left[H^+\right] = \frac{K_w\left(V+v\right)}{B\left(v-v_e\right)} = \frac{1}{\gamma_{H^+}}\ 10^{-\frac{EF}{2.303\,RT}}\ 10^{-\frac{\left(E_o'+E_j\right)F}{2.303\,RT}} \qquad (6)$$

and we may use a similar function defined by

$$\Psi' = \left(V+v\right)\ 10^{\frac{EF}{2.303\,RT}} = \frac{B\left(v-v_e\right)}{K_w\,\gamma_{H^+}}\ 10^{-\frac{\left(E_o'+E_j\right)F}{2.303\,RT}}\ . \qquad (7)$$

If γ_H, E_j and K_w remain constant throughout the titration, then from equations (5) and (7) the quantities Φ' and Ψ' are linear functions of v, such that $\Phi'(v)$, $\Psi'(v)$ and the abscissa all intersect at the point 0, v_e. Thus the value of v_e may be obtained by plotting any one of the quantities Φ' or Ψ' against v, and extrapolating the line obtained to cut the abscissa at the point $v = v_e$.

A *Gran's* plot $\Phi' = \Phi'(v)$ for the titration of wine sample 4 as well as the pH dependence from the volume of base added, v, is shown in figure 1. Similar titration curves and *Gran's* plots were found for all other wine samples. They are all comparable to the potentiometric titration curve and *Gran's* plot of a model mixture of aqueous solutions of some organic acids (Fig. 2). All titration curves, the model and sample ones, were found to show only one inflection point because of the overlapping of several degrees of dissociation of organic acids. In the case of wine samples, indeed a small deviation from linearity near the equivalence point, v_e can be observed (Fig. 1). It may be due to different factors, e.g. contamination of the real sample with metal ions which form complexes with anions of acids, interference of dissolved carbon dioxide still present in wine sample, etc. But the beauty of a *Gran's* plot is that only a few points are needed on the straight line at some distance away from the end point. However, a perfect linear fit of the theoretical curve to the experimental points (see Fig. 1) enables us to find the end point in the potentiometric titration of wine samples in a very simple way.

In tables I and II the data for the wine samples investigated are presented. On the basis of the experimental results shown in table I, it is evident that the density of these wine samples is about 1 g cm^{-3}, a value that is characteristic for dry wines [12]. Moreover, the lower values of refractive index for samples from 1 to 8 and the higher ones for samples from 9 to 20 indicate corresponding sugar contents, i.e. they confirm the samples are dry and medium dry, res-

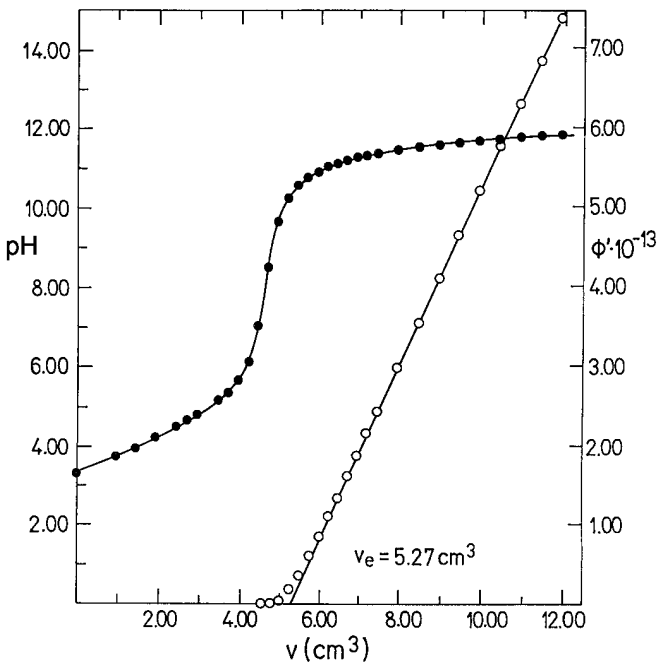

Fig. 1. Titration of 5 cm^3 of wine (sample 4) + 100 cm^3 H_2O with NaOH (c = 0.1 mol dm^{-3}). Change in pH and Φ' with volume of base added, v (cm^3); pH_e = 10.26, c = 0.1044 mol dm^{-3}.

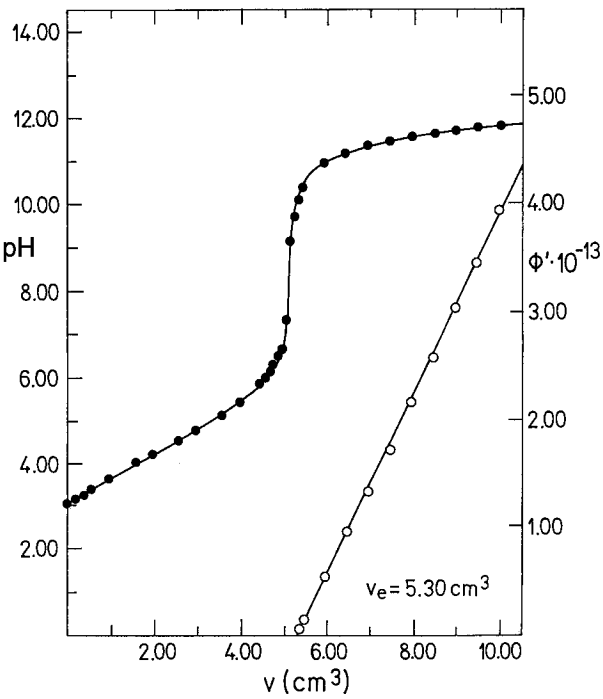

Fig. 2. Titration of 5 cm^3 of model mixture (aqueous solutions of acetic, tartaric, malic, succinic and citric acid) + 100 cm^3 H_2O with KOH (c = 0.1 mol dm^{-3}). Change in pH and Φ′ with volume of base added, v (cm^3); pH_e = 9.74, c = 0.1055 mol dm^{-3}.

Table I. Density, refractive index, ethanol and extract content of several Slovenian white wine samples at 293 K.

Sample	ρ (*g cm*$^{-3}$)	*ethanol* (*vol. %*)	*extract* (*g dm*$^{-3}$)	n_D
1	0.99295	10.42	22.3	1.3417
2	0.99163	11.39	21.9	1.3422
3	0.99231	11.34	23.6	1.3424
4	0.99119	12.24	23.5	1.3429
5	0.99117	12.34	23.7	1.3430
6	0.98920	12.17	18.0	1.3421
7	0.99075	11.91	20.7	1.3424
8	0.99112	12.26	23.2	1.3429
9	0.99904	9.48	35.1	1.3430
10	1.00071	10.74	43.3	1.3449
11	0.99917	10.91	40.2	1.3445
12	1.00053	11.00	43.8	1.3451
13	0.99663	10.55	32.2	1.3432
14	0.99779	10.82	36.1	1.3439
15	0.99507	11.42	31.1	1.3435
16	0.99606	11.55	33.5	1.3440
17	0.99824	10.85	37.3	1.3441
18	0.99690	11.64	36.4	1.3444
19	0.99746	11.92	38.9	1.3449
20	0.99616	12.00	35.7	1.3445

Table II. Measures of wine acidity of various cultivars and locations in Slovenia at 293 K.

Sample	pH_{sample}	*c* (*mol dm*$^{-3}$)	pH_e	*c** (*mol dm*$^{-3}$)	(*c-c**) 10^3 (*mol dm*$^{-3}$)	*Buffer capacity* (*mmol/dm*^{3}*/pH*)
1	3.121	0.1181	10.24	0.1091	9.0	52.6
2	3.154	0.1042	10.22	0.0970	7.3	46.9
3	3.463	0.1008	10.25	0.0896	11.2	45.2
4	3.142	0.1055	10.26	0.0940	11.5	45.1
5	3.198	0.1079	10.17	0.0981	9.9	49.7
6	3.246	0.0929	10.19	0.0815	11.4	42.2
7	3.230	0.0942	10.08	0.0867	7.5	42.2
8	3.160	0.1104	10.13	0.1005	9.8	47.8
9	3.192	0.1288	10.27	0.1133	15.5	55.4
10	3.073	0.1566	10.16	0.1435	13.1	67.1
11	3.010	0.1170	10.10	0.1080	9.0	51.9
12	3.315	0.1314	10.28	0.1154	16.0	55.1
13	3.101	0.1331	10.08	0.1239	9.2	58.0
14	3.356	0.1289	10.24	0.1156	13.3	55.6
15	3.089	0.1119	10.13	0.1011	10.8	47.1
16	3.298	0.1220	10.22	0.1088	13.2	50.9
17	3.581	0.1275	10.28	0.1136	13.9	55.9
18	3.122	0.1368	10.25	0.1230	13.8	57.4
19	3.178	0.1317	10.30	0.1109	20.8	54.1
20	3.316	0.1096	10.26	0.0932	16.3	45.8

c - total acidity determined by potentiometric titration up to the true end point of pH_e
*c**- total acidity determined by potentiometric titration up to pH 8.2.

pectively. The extract value follows the sugar content in wine samples, although in general, the major components in the extract of dry wines are glycerol and organic acids. The buffer capacities, presented in table II, were calculated on the basis of potentiometric data, i.e. from polynomial dependence (second degree polynomial) of volume of strong base, v (cm^3) on pH of diluted sample. Buffer capacity was expressed as the number of millimoles of strong base per litter needed to produce a unit change in pH and can be seen to vary due to the season, location and cultivar.

On the basis of the data in Table II one can conclude that the total acidity of wine, that measures free H^+ plus any undissociated acids that can be neutralized by base, c, is significantly higher if it is determined on the basis of the true end point, pH_e (which obviously varies with samples) than the total acidity, determined on the basis of the proposed end point pH 8.2. The maximum difference, ($c - c^*$) is 0.0208 mol dm^{-3} which is by no means negligible.

The method we used for titratable acidity determination of wine samples (it can be also be applied to juice or must) was found to be quite simple, reliable and accurate enough ($\delta c = 15 \times 10^{-5}$ mol dm^{-3}) for use in research and routine wine analysis. Namely, *Gran's* plots are quicker than the conventional plots because fewer data points are required, and because electrode response is generally fast at the concentrations needed for extrapolation of measurements. The calculations are quick and easy. Finally, the end points obtained by a linear *Gran's* extrapolation are much more precise than those obtained by the differential method, especially if the titration curve is not symmetrical, as it is exactly the case for wine samples.

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