

# On the Titration of a Weak Acid with a Weak Base: Application to the Potentiometric Determination of the Degree of Acidity of Vinegar

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**Abstract** Although the number of direct instrumental methods of chemical analysis is continuously increased, titrations are still important in routine practice in many laboratories. The aim of this contribution is to carry out the study of weak acid/weak base titration curves, while also emphasizing titration error. A diagram for the titration error in function of the difference between the end and equivalence point ( $pH_{eq}$ ) is drawn in order to facilitate the graphical calculation of titration error. The approach to the construction of redox titration curves, based on the use of a hyperbolic sine expression, is applied here to weak acid/weak base titrations. While the approach in its simplified form is limited by the water ionization, herein we derive a complete expression applicable in all situations when dealing with weak and medium strength acids titrated with weak and medium strength bases. The acetic acid/ammonia system is selected first as example in order to derive the equations, the reaction is studied in detail and applied to the determination of acetic acid (acidity degree) in vinegar.

**Keywords** Weak acid/weak base, Titration curves, Titration error, Vinegar acidity, Potentiometric titrations, Gran method

## 1. Introduction

Titrimetry has been applied since the late 18<sup>th</sup> century and is one of the oldest known methods [1] of chemical analysis. Based on reaction chemistry, it is still developing [2-4] and it plays an important role in various analytical fields as well as routine studies. Among their main advantages are [5-7] its superior speed and simplicity, with little sacrifice in accuracy and precision and its low cost. Titrimetry does not require expensive equipment and measurements are quickly carried out and easily automated.

Together with gravimetry, titrimetry is one of the two primary methods used to determine chemical composition on the basis of chemical reactions [8-9]. Both gravimetry and titrimetry (classical analysis) lead directly to independent values of chemical quantities expressed in S.I. units. The wide-ranging applications combined with the simplicity of the method make titrimetry an attractive method of measurement and it continues to be extensively employed in a wide range of laboratories.

The aim of this contribution is to carry out the study of weak acid/weak bases titration curves including error titration. A method, which allows to draw redox titration curves [5] without piecemeal approximations, based on the use of a hyperbolic sine expression is applied here to weak acid/weak base titrations. While the approach in its simplified form is limited by the water ionization, herein we derive a complete expression applicable in all situations when dealing with weak and medium strength acids titrated with weak and medium strength bases.

The reaction between acetic acid and ammonia is studied in detail, being in addition applied to the determination of acetic acid (acidity degree) in vinegar. The complete method developed here and the equivalent “de Levie” method [10-12] are used as “control methods” in order to check calculations on Excel spreadsheets. Titration error may be expressed as a function of the difference between the end and equivalence ( $pH_{eq}$ ) points [13-14] and a diagram for the titration error is drawn. In spite that acid-base titration curves have received a great attention and numerous papers on this topic may be found in the analytical literature, papers concerning with weak and medium strength acids titrated with weak and medium strength bases are usually scarce.

## 2. Theory: Basic Equations

For the acid/base conjugate pair ammonia / ammonium

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Published online at <http://journal.sapub.org/jlce>

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ion, we have

$$NH_3 + H^+ \rightleftharpoons NH_4^+ \quad K_T = \frac{[NH_4^+]}{[NH_3][H^+]} = 10^{9.35} \quad (1)$$

and for the acetate / acetic acid pair

$$CH_3COO^- + H^+ \rightleftharpoons CH_3COOH \quad K_S = \frac{[CH_3COOH]}{[CH_3COO^-][H^+]} = 10^{4.65} \quad (2)$$

The titration reaction of acetic acid by ammonia is given by



being its equilibrium constant, as a function of the previous ones,  $K_T$  and  $K_S$

$$K_{eq} = \frac{[CH_3COO^-][NH_4^+]}{[CH_3COOH][NH_3]} = \frac{K_T}{K_S} = \frac{10^{9.35}}{10^{4.65}} = 10^{4.7} \quad (4)$$

From Eq. (3) it is readily seen that in any moment of the titration it holds that (through the entire concentration range)

$$[NH_4^+] = [CH_3COO^-] \quad (5)$$

On the other hand, we may define the (relative) titration error as

$$\Delta T = \left( \frac{C_T - C_S}{C_S} \right) = \frac{[NH_3] - [CH_3COOH]}{C_S} = T - 1 \quad (6)$$

where  $C_T = [NH_3] + [NH_4^+]$  and  $C_S = [CH_3COOH] + [CH_3COO^-]$  are the analytical concentrations of titrant and analyte, respectively, and  $T = (V_T C_T)/(V_S C_S)$ , the fraction titrated, is defined as the ratio between the amount of titrant added and the initial amount of analyte at any moment of the titration ( $V_S$  is the initial volume of acetic acid solution and  $V_T$  the volume of titrant added). Thus, depending on the nature of the titration,  $\Delta T$  might be either positive or negative. When the titration is carried out in the reverse order the same result is obtained, but the equation now bears a minus sign.

By combining Eqs. (1) and (5) we have

$$[NH_3] = \frac{[NH_4^+]}{K_T [H^+]} = \frac{[CH_3COO^-]}{K_T [H^+]} \quad (7)$$

and from Eq. (2) we obtain

$$[CH_3COOH] = K_S [CH_3COO^-][H^+] \quad (8)$$

By substituting the values of  $[NH_3]$  and  $[CH_3COO^-]$  given by Eqs. (7) and (8) in Eq. (6) we get

$$\Delta T = \frac{1}{1 + K_S [H^+]} \left( \frac{1}{K_T [H^+]} - K_S [H^+] \right) \quad (9)$$

as the molarity fraction of the species  $CH_3COO^-$  is given by

$$f_s = \frac{[CH_3COO^-]}{C_S} = \frac{1}{1 + K_S [H^+]} \quad (10)$$

By multiplying and dividing the right hand of Eq. (9) by  $\sqrt{(K_S/K_T)}$  we get

$$\Delta T = \frac{\sqrt{\frac{K_S}{K_T}}}{1 + K_S [H^+]} \left( \frac{1}{\sqrt{K_T K_S} [H^+]} - \sqrt{K_T K_S} [H^+] \right) \quad (11)$$

In the equivalence point, when the exact stoichiometric amount of titrant has been added, in addition to Eq. (5), the following condition is satisfied

$$[CH_3COOH] = [NH_3] \quad (12)$$

and then, from Eqs. (1) and (2) it follows that when the exact stoichiometric amount of titrant has been added

$$[H]_{eq} = \frac{1}{\sqrt{K_T K_S}} \quad (13)$$

$$pH_{eq} = \frac{\log K_T + \log K_S}{2} \quad (14)$$

The  $pH$  at the equivalence point is independent of the concentration of the reactants and thus unaffected by dilution. Note, however, that Eq. (13) is not perfectly general. The simple relation of Eq. (5) for reactants and products is not always valid because it simplified the electroneutrality rule, given by

$$[H^+] + [NH_4^+] = [OH^-] + [CH_3COO^-] \quad (15)$$

By substituting expression (13) in Eq. (11)

$$\Delta T = \frac{\sqrt{\frac{K_S}{K_T}}}{1 + K_S [H^+]} \left( \frac{[H^+]_{eq}}{[H^+]} - \frac{[H^+]}{[H^+]_{eq}} \right) \quad (16)$$

The difference between the end point and the equivalence point leads to a systematic error of determination. Setting

$$\Delta pH = pH - pH_{eq} \quad (17)$$

and taken into account the definition of hyperbolic sine

$$\sinh x = \frac{e^x - e^{-x}}{2} \quad (18)$$

after some manipulation, the following expression may be easily obtained

$$\Delta T = \frac{2\sqrt{\frac{K_S}{K_T}}}{1 + K_S [H^+]} \sinh(\ln 10 \cdot \Delta pH) \quad (19)$$

Note that when we applied Eq. (19), the titration curve  $T = f(pH)$  depends only on  $pK_a$ 's of two given pairs, being independent of the analyte and titrant concentrations.

For a rigorous treatment, however, from Eq. (15) we have

$$\begin{aligned} [NH_4^+] &= [CH_3COO^-] - ([H^+] - [OH^-]) \\ &= [CH_3COO^-] - \Delta \end{aligned} \quad (20)$$

and applying again the entire treatment we get

$$\begin{aligned} \Delta T &= \frac{1}{1 + K_s[H^+]} \left( \frac{1}{K_T[H^+]} - K_s[H^+] \right) \\ &\quad \frac{\Delta \left( \frac{1}{K_T[H^+]} + 1 \right)}{C_{CH_3COOH}} \end{aligned} \quad (21)$$

The first part of the right hand of Eq. (21) coincides virtually with Eq. (19) as equivalence point is practically unaffected by dilution and  $pK_a$ .

So, the titration error,  $\Delta T$ , and titration curves

$$T = \Delta T + 1 \quad (22)$$

may be formulated as a hyperbolic sine expression. Hyperbolic functions are of great worth in parameter estimation as shown in [15]. The expression for the titration curve without approximations on the basis of Eq. (21) is equivalent to the procedure described by “the Levie” [10-12], and both expressions are used in this contribution for the sake of checking and comparison.

### 3. Weak Acids/Weak Bases Titration Curves

Equation (19) is first used to draw the titration curves of acetic acid ( $pK_a = \log K_s = 4.65$ ) with ammonia ( $pK_a = \log K_T = 9.35$ ) as titrant, by applying

$$\begin{aligned} \Delta T &= \frac{\sqrt[2]{\frac{K_s}{K_T}}}{1 + [H^+] K_s} \sinh(\ln 10(pH - pH_{eq})) = \\ &= \frac{\sqrt[2]{\frac{10^{4.65}}{10^{9.35}}}}{1 + 10^{-pH} \cdot 10^{4.65}} \sinh(2.303(pH - 7)) = \\ &= \frac{8.934 \cdot 10^{-3}}{1 + 10^{4.65-pH}} \sinh(2.303(pH - 7)) \end{aligned} \quad (23)$$

Since the  $pX_{eq}$  according to Eq. (14) is equal to  $(\log K_T + \log K_s) / 2 = (9.35 + 4.65) / 2 = 7$ . As a matter of fact this result is the fundament of the use of ammonium acetate as a buffer to regulate  $pH$  in the neutral zone. Figure 1 shows also titration curves for two other stronger acids of  $pK_a$  2.90 and 1.45, respectively. Titration curves show three points of inflection, at fractions titrated values of  $T = 0$  (beginning of titration),  $T = 0.5$  (half point titration) and  $T = 1$  (equivalence point titrations). Note that in this titration  $pH_{1/2} = pK_a(HA)$  and  $pH_{3/2} = pK_a(NH_4^+)$ .

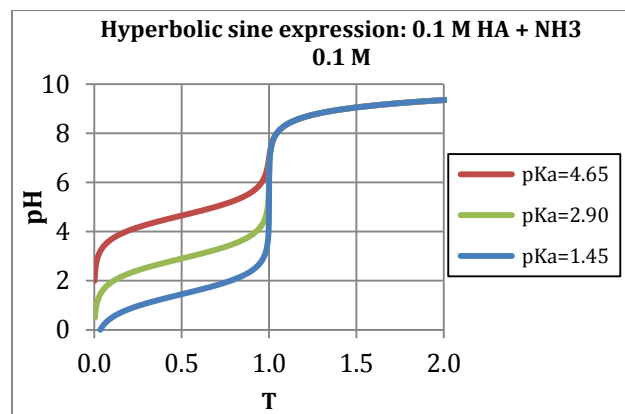


Figure 1. Theoretical titration curves drawn with the function described by Eq. (19)

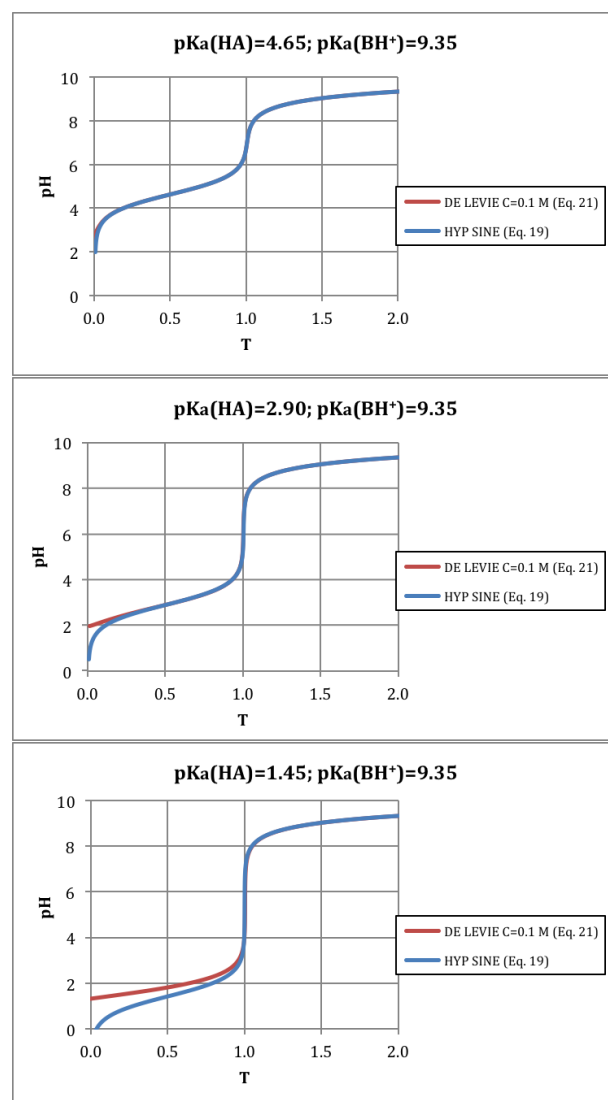
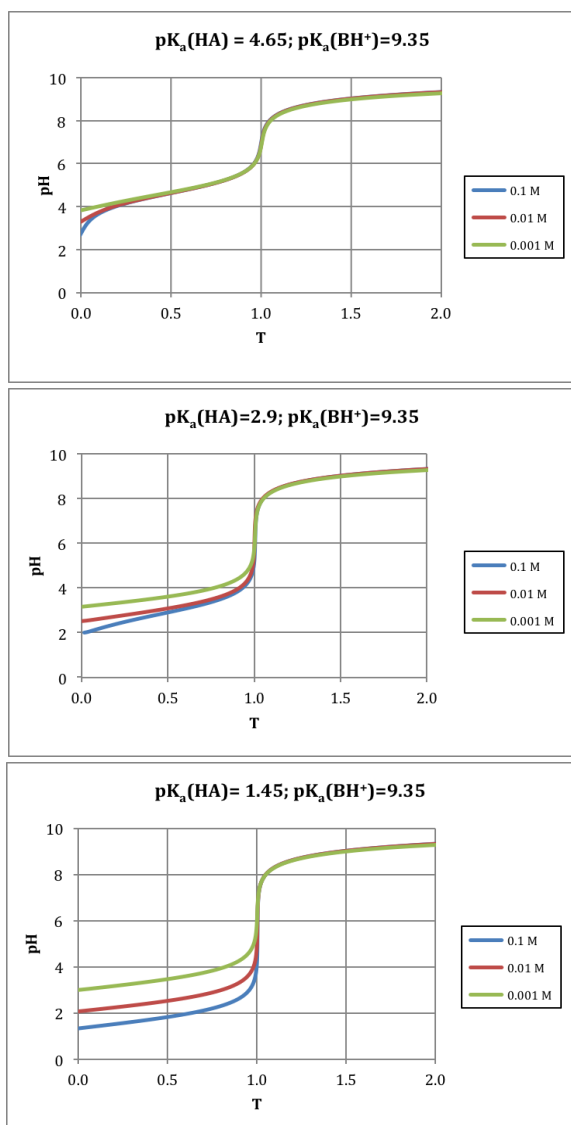


Figure 2. Titration of 0.1 M acids of  $pK_a = 4.65$ , 2.90 and 1.45 with a 0.1 M base of  $pK_a = 9.35$  (i.e. ammonia)

Figure 2 shows the acid titration curves for acids with different strengths,  $pK_a = 4.65$ , 2.90 and 1.45, at the same concentration (0.1 M), titrated with a base of  $pK_a = 9.35$  ( $pK_b = 4.65$ ) and at a concentration equal to 0.1 M. For the sake of

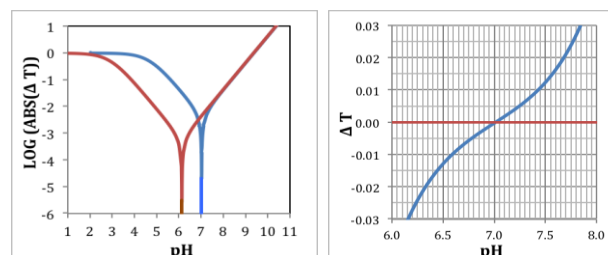
comparison, the calculus using the function of hyperbolic sine given by Eq. (19) are presented in blue and those using the rigorous method given by Eq. (21), equivalent to "de Levie" method in red. The shapes of the curves are identical after the equivalence point, and for acids of middle strong ( $pK_a = 2.90$ ) and weak acids ( $pK_a = 4.65$ ), the curves closely match except in the beginning. The stronger the acid, the curves far more before the equivalence point from the hyperbolic sine model described by Eq. (19).

Figure 3 shows the effect of concentration on the curve shape. Acid titration curves of  $pK_a = 4.65$ , 2.90 and 1.45, evaluated with a base of  $pK_a = 9.35$ , both at concentrations of 0.1, 0.01 and 0.001 M are drawn. It is observed that the titration curves corresponding to the acid of  $pK_a = 4.65$  are practically coincident, except at the beginning. As the acid strength increases, that is, its  $pK_a$  decreases, the difference between the curves calculated by the (simplified) hyperbolic sine method (Eq. 19) and the complete method (Eq. 21) becomes more evident.



**Figure 3.** Titration of 0.1, 0.01, and 0.001 M acids of  $pK_a = 4.65$ , 2.90 and 1.45 with a 0.1, 0.01 and 0.001 M base of  $pK_a = 9.35$  (i.e. ammonia)

Figure 4 left shows a logarithmic diagram of the titration error for acids with  $pK_a = 4.65$  and 2.90, throughout the titration interval. Note that when the error is zero ( $\Delta T = 0$ ),  $\log(\text{ABS}(\Delta T)) = -\infty$ . A conventional diagram for the calculation of the acid titration error with  $pK_a = 4.65$  is shown in Figure 4 right. Both diagrams are based on the described hyperbolic sine function.



**Figure 4.** Left: Logarithmic plot of the titration error for acids with  $pK_a = 4.65$  (blue line) and 2.90 (red line). Right: Titration error diagram  $\Delta T = f(\text{pH})$  (in the environment of  $\pm 3\%$ );  $pK_a = 4.65$

## 4. Experimental Part. Determination of the Degree of Acidity of Commercial (Wine) Vinegar

Article 3.1 of Spanish Royal Decree 661/2012 of April 13 (BOE No. 100 of April 23, 2012) defines vinegar [16] as "the liquid suitable for human consumption resulting from the double alcoholic and acetic fermentation of products of agricultural origin". Wine vinegar is the product obtained exclusively by acetic fermentation of wine (article 3.3, RD 661/2012) [16-19]. Vinegar is a product obtained by the oxidation of ethanol contained in alcoholic beverages of low graduation thanks to the action of microorganisms (acetic bacteria). It contains different organic acids, mainly acetic acid, and other components such as sulphates, chlorides, sulphur dioxide, etc. Total acidity or acetic grade is a quality index, and is defined as all the volatile and fixed acids contained in vinegar expressed in grams of acetic acid in 100 ml of vinegar (acidity degree), i.e. % w / V. It can be determined by titration with a solution of a base of known concentration. Spanish legislation provides that commercial vinegars must contain at least 60 grams of acetic acid per liter (6% w/V) for wine vinegars. That is, commercial wine vinegars must have an approximate concentration of 1 M acetic acid. For other kind of vinegars, the minimum concentration required is 50 g/L acetic acid.

### Apparatus and Reagents

- pH-meter Crison GLP 21, with a combined Ag / AgCl glass electrode. The pH meter is calibrated (three-point method) using the pH 4.01, 7.00 and 9.21 buffers. Calibration is repeated at the beginning of each series of titrations. Five mL burettes (Brand) ( $\pm 0.01$  at 20 °C) and 50 mL burettes (Brand) ( $\pm 0.1$  at 20 °C). Adjustable volume micropipettes 100-1000  $\mu\text{L}$ , and 1000-5000  $\mu\text{L}$  (Hamilton).

Acetic acid ( $\text{C}_2\text{H}_4\text{O}_2$ )  $M = 60 \text{ g/mol}$  (Merck > 99.5%, 1.049 g/mL); Ammonia in 30% solution  $M = 17.03 \text{ g/mol}$

(Panreac, p.a.); Sherry vinegar (7.5 %); Potassium hydrogen phthalate ( $\text{C}_8\text{H}_5\text{KO}_4$ )  $M = 204.22 \text{ g/mol}$  (Merck, analytical grade); Water for ACS analysis (Panreac).

#### Solutions

- 0.100 M acetic acid: 1.573 mL of commercial acetic acid is taken and the solution is transferred to a 250 mL volumetric flask and diluted with distilled water to the mark.

- 0.100 M Ammonia: 1.582 mL of commercial ammonia solution is taken and transferred to a 250 mL volumetric flask and diluted with distilled water to the mark.

#### Experimental procedure: Titration of acetic acid

20.0 mL of the 0.100 M acetic acid solution is pipetted. The contents of this solution are transferred to a 200 mL beaker, and the solution is titrated with a freshly prepared ammonia solution of 0.095 M ammonia (previously standardized with potassium hydrogen phthalate) with a burette of 50.0 mL. The pH readings are performed with the pH-meter Crison GLP 21 (Figure 5). Two titrations were made. The results obtained in the first one are drawn in Figure 6.



Figure 5. Device used in potentiometric titration

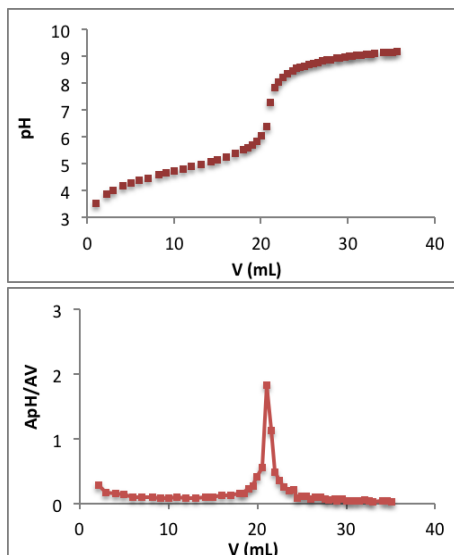


Figure 6. Top: titration curve of 20.0 mL of 0.100 M acetic acid with ammonia. Bottom: first derivative

#### Titration of vinegar

0.30 mL of Sherry vinegar is pipetted. The contents of this solution are transferred to a 100 mL beaker, 50 mL of water are added and the solution is titrated with a freshly prepared ammonia solution 0.095 M (previously standardized with potassium hydrogen phthalate) with a 5.00 mL burette. The pH readings are performed with the pH-meter Crison GLP 21. The shapes of titration curves of the vinegar are similar to the titration curves of acetic acid. Results are obtained in triplicate in this case. Details of the second titration [V, pH] data follows: [0.00, 3.377]; [0.10, 3.417]; [0.20, 3.506]; [0.32, 3.603]; [0.40, 3.654]; [0.50, 3.750]; [0.60, 3.843]; [0.70, 3.889]; [0.80, 3.974]; [0.90, 4.048]; [1.00, 4.118]; [1.10, 4.180]; [1.20, 4.217]; [1.33, 4.298]; [1.40, 4.33]; [1.50, 4.391]; [1.60, 4.451]; [1.70, 4.480]; [1.80, 4.541]; [1.90, 4.598]; [2.00, 4.626]; [2.10, 4.684]; [2.20, 4.742]; [2.30, 4.771]; [2.40, 4.828]; [2.50, 4.885]; [2.60, 4.911]; [2.72, 5.004]; [2.80, 5.037]; [2.90, 5.103]; [3.00, 5.137]; [3.10, 5.211]; [3.20, 5.252]; [3.30, 5.361]; [3.40, 5.518]; [3.50, 5.518]; [3.60, 5.65]; [3.70, 5.807]; [3.80, 6.036]; [3.90, 6.220]; [4.00, 6.885]; [4.10, 7.576]; [4.20, 7.896]; [4.30, 8.012]; [4.42, 8.212]; [4.50, 8.120]; [4.60, 8.369]; [4.70, 8.444]; [4.80, 8.480]; [4.90, 8.546]; [5.00, 8.599]. The results are given with three decimal digits in order to show the precision of measurements achieved even if they are not significant.

## 5. Determination of the End Point: Method of the First Derivative

Calculate the quotient of the pH increments between the volume increments and plot against the semi-sum of the pH values

$$\frac{\Delta pH}{\Delta V} = \frac{pH_n - pH_{n-1}}{V_n - V_{n-1}} = f\left(\frac{V_n + V_{n-1}}{2}\right) \quad (24)$$

The equivalence point coincides practically with a point of inflection in the curve, so that its second derivative is zero, and the first one a maximum, since it is titrated an acid with a base (or a minimum for the inverse reaction, when a base is titrated with an acid). This method requires many points in the vicinity of the end point, in order to assimilate the increments to its derivative. When falling near the zero of potentiometer, the measurements fluctuate, being high the variations of pH, affecting adversely the accuracy. To avoid these drawbacks we resort to methods that do not depend on the results at the end point, but along the titration curve, as we will see in next section.

## 6. Determination of the End Point: Gran Linearization Method [20]

When the acetic acid is titrated with the ammonia according to Eq. (3), prior to the equivalence point, from Eq. (2) we get

$$K_S = \frac{[CH_3COOH]}{[CH_3COO^-][H^+]} = \frac{C_S V_0 - C_T V_T}{C_T V_T [H^+]} \quad (25)$$

and bearing in mind that

$$C_S V_0 = C_T V_{eq} \quad (26)$$

we get

$$K_S = \frac{V_{eq} - V_T}{V_T [H^+]} \quad (27)$$

which on rearrangement gives

$$V_T [H^+] = \frac{V_{eq}}{K_S} - \frac{V_T}{K_S} = K_{a(HA)} V_{eq} - K_{a(HA)} V_T \quad (28)$$

The representation of  $V_T [H^+]$  versus  $V_T$  gives rise to a straight line,  $y = a_0 + a_1 x$ , whose cut-off point on the x-axis coincides with the estimated volume at the equivalence point

$$V_{eq} = -\frac{a_0}{a_1} \quad (29)$$

The apparent value of  $pK_a$  (HA) (acetic acid) can be estimated from the slope of the corresponding straight line ( $a_1 = -K_a$ )

$$pK_{a(HA)} = -\log K_a = -\log(-a_1) \quad (30)$$

After the equivalence point comes into play the ammonia-ammonia pair (Eq. 1)

$$K_T = \frac{[NH_4^+]}{[NH_3][H^+]} = \frac{C_T V_T}{(C_T V_T - C_S V_0)[H^+]} \quad (31)$$

$$= \frac{V_T}{(V_T - V_{eq})[H^+]}$$

on rearrangement leads to

$$\frac{V_T}{[H^+]} = K_T (V_T - V_{eq}) = \frac{1}{K_{a(BH^+)}} (V_T - V_{eq}) \quad (32)$$

A representation of the term on the left,  $V_T / [H^+]$  versus  $V_T$  gives a straight line whose cut-off point with the x-axis is an estimate of  $V_{eq} = -a_0 / a_1$ , and whose slope is equal to the inverse of acid constant of the ammonium ion ( $BH^+$ ), which has

$$pK_{a(BH^+)} = \log a_1 \quad (33)$$

In Gran method, therefore, points before and after (distanced) of the equivalence point are used, preferably in the buffer zone where appreciable quantities of the species composing the acid-conjugate pair coexist. Note however that the object of the Gran method is the determination of the end point of the titration, nor the calculation of the acidity constants. In this last case, an accurate knowledge of the acid and base concentrations used in the titration would require as well as a different rearrangement from the titration parameters, in order to obtain the value of  $pK_a$  as a cut-off point with the x-axis (a quotient intercept/slope method), and not as an intercept extrapolation method.

## 7. Results and Discussion

The results of the Gran (and first derivative) method are shown in Table 1. To the end point volume data obtained the Q test of Dixon and G test of Grubbs are applied [21-23], dropping the 21.8 value, since  $Q_{exp} = 0.667 > Q_{tab(0.95,6)}$  and  $G_{exp} = 1.916 > G_{tab(0.95,6)} = 1.887$ . An end point volume of  $21.0 \pm 0.1$  mL is obtained, which corresponds to  $0.0952 \pm 0.0006$  M in ammonia. Results obtained by the Gran and first derivative methods in the titration of vinegar with ammonia are shown in Table 2 and Figure 7. The Dixon and Grubbs tests do not rule out any data, resulting in an end point of  $3.98 \pm 0.11$  mL and a % w/v of acetic acid of  $7.57 \pm 0.22$ . The  $pK_a$  values of  $CH_3COOH$  and  $NH_4^+$  at  $I = 0.1$  are equal to 4.629 (4.760) and 9.318 (9.250), respectively. Note the proximity of  $pK_a$  values obtained in this contribution to these  $pK_a$  values (except for acetic with ammonia in the basic range). Approximate single point method  $pH_{1/2}$  gives 4.684 for acetic acid  $pK_a$ .

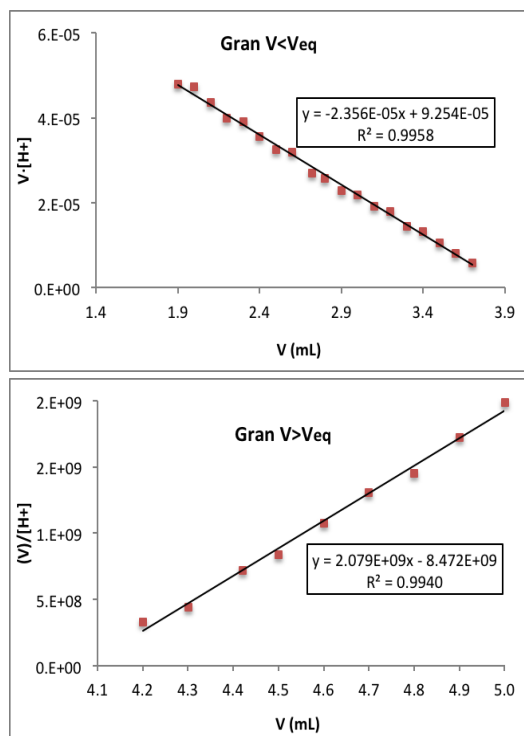
**Table 1.** Gran method applied to the titration of acetic acid with ammonia

pH Range	V Range	N° Points	V End Point	$pK_a$ (HAc)	$pK_a$ ( $NH_4^+$ )	1° der. End Point
Acid	7.0-20.6	17	21.2	4.771	-	
Basic	22.0-33.0	23	20.9	-	9.558	21.1
Acid	8.0-20.0	15	20.9	4.676	-	
Basic	22.0-13.0	23	21.8	-	9.530	21.0

**Table 2.** Gran method applied to the titration of Sherry vinegar with ammonia

pH Range	V Range	N° Points	V End Point	$pK_a$ (HAc)	$pK_a$ ( $NH_4^+$ )	1° der. End Point
Acid	1.70-3.82	22	3.93	4.583	-	4.10
Basic	4.20-5.00	9	3.93	-	9.312	
Acid	1.90-3.70	19	3.77	4.629	-	4.05
Basic	4.20-5.00	9	4.11	-	9.318	
Acid	2.50-3.70	13	4.08	4.511	-	3.90
Basic	4.10-5.00	10	3.94	-	9.283	





**Figure 7.** Gran method applied to the evaluation of a sherry vinegar with ammonia: sample # 2. Upper part: range of acid pH values, Eq. (28). Bottom: range of basic pH values, Eq. (32)

## 8. Final Comments

A method for the calculation of titration curves and titration error in weak acids/weak bases titrations reactions has been devised. The hyperbolic sine expression formulated is compact and allows calculating the entire titration curve without piecemeal approximations. A diagram for the titration error in function of the difference between the end and equivalence point ( $\Delta pH$ ) is drawn in order to facilitate the graphical calculation of titration error. All calculations involved have been checked, for the sake of comparison, with a rigorous method proposed [10-12] by “de Levie”, and no differences were found in the numerical values obtained by both methods. The titration curves in the case of weak acid-weak base systems proves to be very useful because their shapes are independent-concentration, thus allowing to carry out the determinations without necessity of previous dilution.

The acetic acid/ ammonia system has been studied in detail, and an application to the determination of acetic acid in vinegar is described. Gran method is easy to automatize and it constitutes a way of  $pK_a$  determination of the acid-base systems involved (ionic strength should be maintained constant through titration) without even a prior knowledge of the concentrations. Ammonia solution may possess volatility problems and it could therefore be replaced by a less volatile diethylamine, which has a  $pK_a$  value of 8.95 [24].

## ACKNOWLEDGEMENTS

Thanks are due to the University of Seville for the concession of a Grant destined to the publication of the Bachelor's degree Final Projects of students.

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