

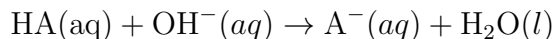
Acid–Base Reactions: Finding the Identity of an Unknown Weak Acid

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ABSTRACT. This experiment identified an unknown monoprotic weak acid through potentiometric titration with a standardized sodium hydroxide (NaOH) solution. The NaOH titrant was first standardized against potassium hydrogen phthalate (KHP), yielding a concentration of 0.1065 ± 0.0011 M (95% CI). The unknown acid was then titrated with the standardized base, producing sigmoidal pH curves characteristic of weak acid–strong base titrations. The equivalence point was determined using both the derivative method and Gran plot analysis. The derivative method, which identifies the inflection point through first and second derivatives, provided more consistent results with trial-to-trial agreement within 0.5%, and further calculations were computed with the derivative method. From the equivalence volumes, the molar mass of the unknown acid was calculated to be 147 ± 8 g mol⁻¹ (95% CI). The pK_a, determined from the pH at the half-equivalence point, was 3.50 ± 0.06 (95% CI). Based on these experimental values, the unknown acid was identified as mandelic acid (literature: MW = 152.15 g mol⁻¹, pK_a = 3.41).

INTRODUCTION

Acid–base titrations are a fundamental analytical technique used to quantify acidic and/or basic species and determine properties such as molar mass and dissociation constants.^{1, 2} In this experiment, two types of titration methods were used: an indicator titration for standardizing a sodium hydroxide (NaOH) solution, and a potentiometric titration using a calibrated pH electrode to generate a full titration curve. These techniques are grounded in the neutralization reaction between a monoprotic weak acid (HA) and a strong base (OH⁻):



Here, the conjugate base (A⁻) dominates the pH at the equivalence point.

The purpose of this experiment was to identify an unknown monoprotic weak acid by determining its molar mass and acid dissociation constant

(pK_a) from its titration curve. Different weak acids have distinct dissociation constants and molar masses; so combining both measurements allows for reliable identification from the list of possible weak acids.¹

To conduct the experiment accurately, several components of the techniques were required. The sodium hydroxide (NaOH) titrant had to be prepared in degassed water to prevent carbon dioxide (CO₂) contamination, which would otherwise form carbonic acid (H₂CO₃) and alter the effective concentration of the base¹. The sodium hydroxide (NaOH) solution was then standardized against potassium hydrogen phthalate (KHP), which is a primary standard that provides reproducible neutralization based on its known molar mass. For the potentiometric portion, the pH electrode was calibrated using pH 4, 7, and 10 as buffers to ensure accurate voltage-to-pH conversion across the entire titration range.

The collected titration data provide insight

into the identity of the unknown acid in several ways. The equivalence point, determined from derivative analysis and/or a Gran plot, gives the number of moles of acid in the sample, which, combined with the measured mass, allows for the calculation of its molar mass. The half-equivalence point yields a pH equal to the acid's dissociation constant (pK_a). Together, these values can be directly compared to known weak acids, allowing for confident identification of the unknown acid.

MATERIALS

The equipment used in this experiment included a 50 mL buret, analytical balance, ring stand with buret clamp, magnetic stir plate, 1-inch stir bar, 10 mL graduated cylinder, 125 mL and 250 mL Erlenmeyer flasks, 250 mL beakers, and a LabQuest2 pH meter with a pH electrode. The chemical reagents used were potassium hydrogen phthalate (KHP), 6 M sodium hydroxide (NaOH), distilled water (H_2O), phenolphthalein indicator, and an unknown monoprotic weak acid provided by the stockroom.¹

METHODS

To prepare the titrant, a sodium hydroxide solution (NaOH) of approximately 0.1 M was made by diluting a small volume of 6 M NaOH into freshly degassed distilled water. The degassed water was created by boiling it to remove dissolved CO_2 , preventing the formation of carbonic acid that would otherwise superficially lower the effective NaOH concentration. The NaOH solution was standardized by accurately weighing 3 samples of approximately 0.4 gram samples of KHP to the phenolphthalein endpoint, allowing calculation of the precise molarity of the base through the equation:

$$M_{NaOH} = \frac{\text{mol KHP} \times (1000 \text{ mL/L})}{\text{mL NaOH added}}$$

To ensure accurate molarity measurements, the initial titration was done at a minimum of three times, with an agreement of $\pm 0.5\%$.

A preliminary titration of the unknown acid was then performed to estimate its molar mass and determine the amount of sample needed to produce an equivalence point near 30 mL. For the potentiometric titration, the pH electrode was calibrated using pH 4, 7, and 10 buffer solutions to ensure accurate voltage-to-pH conversion. The weighed unknown acid was dissolved in distilled water and titrated with the standardized NaOH while being continuously stirred, with pH measured after each incremental addition of base. Smaller volume additions were used near the steep region of the titration curve to accurately identify the equivalence point. The resulting titration curve provided the equivalence volume and half-equivalence pH, which were used to calculate the molar mass and pK_a of the unknown acid for identification.¹

RESULTS

Standardization of NaOH Solution

The sodium hydroxide (NaOH) titrant was standardized using potassium hydrogen phthalate (KHP), a primary monoprotic acid standard. Four titrations were performed, but Trial 1 deviated by more than 1.5% from subsequent trials and was excluded. Trials 2, 3, and 4 showed acceptable agreement ($< 0.5\%$ deviation) and were used for the final calculation. Table 1 summarizes the standardization data.

Table 1: Standardization of NaOH with KHP

Trial	Mass (g)	Vol (mL)	[NaOH] (M)
2	0.4017	18.4	0.1069
3	0.4103	18.9	0.1060
4	0.4055	18.6	0.1064
Avg $\pm$ 95% CI:			0.1065 $\pm$ 0.0011

For each trial, moles of KHP were calculated:

$$n_{KHP} = \frac{m_{KHP}}{M_{KHP}}, \quad M_{KHP} = 204.22 \text{ g mol}^{-1}$$

Since KHP is monoprotic, $n_{NaOH} = n_{KHP}$. Molarity:

$$M_{NaOH} = \frac{n_{NaOH}}{V_{NaOH}}$$

Sample Calculation (Trial 2):

$$n_{\text{KHP}} = \frac{0.4017 \text{ g}}{204.22 \text{ g mol}^{-1}} = 0.001967 \text{ mol}$$

$$M_{\text{NaOH}} = \frac{0.001967 \text{ mol}}{0.0184 \text{ L}} = 0.1069 \text{ M}$$

Average calculated as $\bar{x} = \frac{1}{n} \sum x_i$, std. dev. as $s = \sqrt{\frac{1}{n-1} \sum (x_i - \bar{x})^2}$. Using $t = 4.303$ for 95% CI:

$$M_{\text{NaOH}} = 0.1065 \pm 0.0011 \text{ M (95\% CI)}$$

Potentiometric Titration of Unknown Acid Preliminary Indicator Titration

A preliminary titration estimated the unknown acid's molar mass. A 0.1333 g sample required 8.80 mL of 0.1065 M NaOH to reach the phenolphthalein endpoint, yielding an estimated molar mass of 142 g mol^{-1} .

Potentiometric Titration Curves

Three potentiometric titrations were performed using the standardized NaOH solution. Figure 1 displays all three titration curves, showing characteristic sigmoidal behavior for monoprotic weak acids.

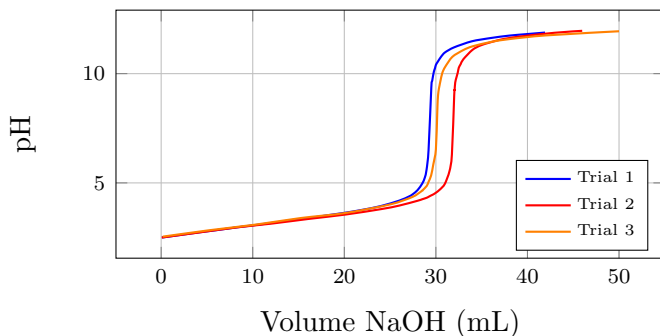


Figure 1: Titration curves showing sigmoidal behavior characteristic of monoprotic weak acids.

Determination of Equivalence Point

The equivalence point for each titration was determined using two methods: the derivative method and the Gran plot method.²

Derivative Method.² The first derivative $\frac{dpH}{dV}$ was calculated between consecutive data points:

$$\left(\frac{dpH}{dV}\right)_i = \frac{pH_{i+1} - pH_i}{V_{i+1} - V_i}$$

The second derivative identifies the inflection point where $\frac{d^2pH}{dV^2}$ crosses zero:

$$\left(\frac{d^2pH}{dV^2}\right)_i = \frac{\left(\frac{dpH}{dV}\right)_{i+1} - \left(\frac{dpH}{dV}\right)_i}{V_{i+1} - V_i}$$

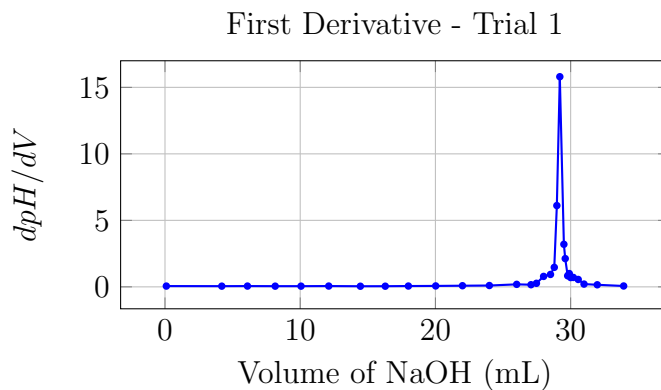


Figure 2: First derivative of the titration curve (Trial 1). The maximum occurs near the equivalence point.

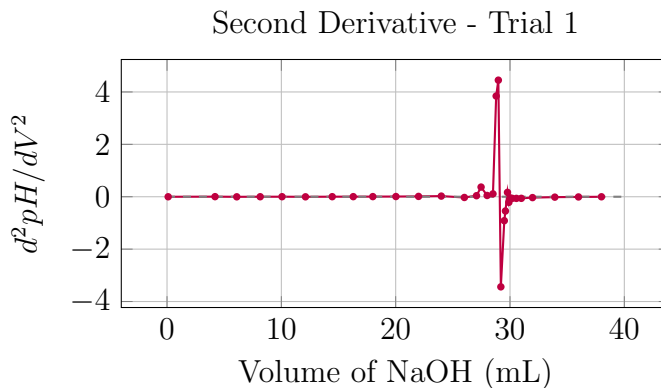


Figure 3: Second derivative of the titration curve (Trial 1). The equivalence point occurs where the curve crosses zero (at approximately 29.2 mL).

Gran Plot Method.² The Gran function linearizes the pre-equivalence region:

$$G_i = V_i \cdot 10^{-pH_i}$$

Linear regression of G_i vs. V_i gives the equivalence volume as the x-intercept: $V_{\text{eq}} = -b/m$.

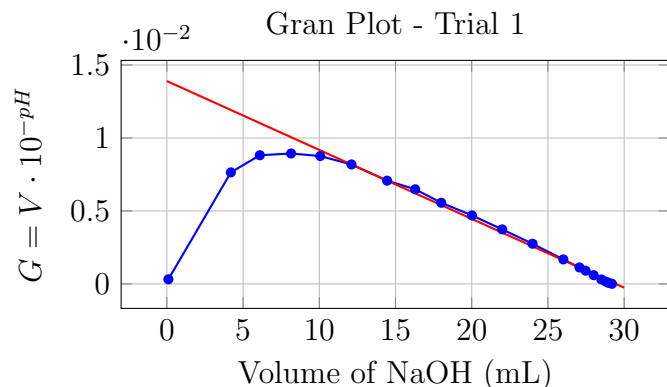


Figure 4: Gran plot (Trial 1) with linear regression. The x-intercept gives $V_{\text{eq}} = 29.2$ mL.

Table 2: Equivalence Points from Derivative and Gran Plot Methods

Trial	V_{eq} Deri.(mL)	V_{eq} Gran(mL)	Mass Acid(g)
1	30.2	29.2	0.4625
2	29.7	31.2	0.4892
3	30.3	30.0	0.4601

The derivative method showed excellent agreement across all three trials ($< 0.5\%$ deviation). Values from the derivative method were used for subsequent calculations.

Molar Mass Determination

The molar mass of the unknown acid was calculated from the equivalence volume using:

$$n_{\text{acid}} = M_{\text{NaOH}} \times V_{\text{eq}}, \quad M_{\text{unknown}} = \frac{m_{\text{sample}}}{n_{\text{acid}}}$$

Sample Calculation (Trial 1):

$$n_{\text{acid}} = (0.1065 \text{ M})(0.0302 \text{ L}) = 0.00322 \text{ mol}$$

$$M_{\text{unknown}} = \frac{0.4625 \text{ g}}{0.00322 \text{ mol}} = 144 \text{ g mol}^{-1}$$

Table 3: Molar Mass Calculations

Trial	V_{eq} (mL)	n_{acid} (mol)	Mass (g)	MW (g/mol)
1	30.2	0.00322	0.4625	144
2	29.7	0.00316	0.4892	155
3	30.3	0.00323	0.4601	143

Using $t = 4.303$ for 95% CI ($n = 3$):

$$M_{\text{unknown}} = 147 \pm 8 \text{ g mol}^{-1} \text{ (95\% CI)}$$

Determination of pK_a

At the half-equivalence point, the concentrations of the weak acid (HA) and its conjugate base (A^-) are equal, so the pH equals the pK_a . The acid dissociation constant was determined from the pH at the half-equivalence point:

$$V_{1/2} = \frac{V_{\text{eq}}}{2}, \quad \text{pK}_a = \text{pH}(V_{1/2})$$

pH values were interpolated from the titration curves.

Table 4: pK_a Determination

Trial	V_{eq} (mL)	$V_{1/2}$ (mL)	pK_a
1	30.2	15.1	3.47
2	29.7	14.85	3.52
3	30.3	15.15	3.50
Avg $\pm$ 95% CI:			3.50 $\pm$ 0.04

Final result:

$$\text{pK}_a = 3.50 \pm 0.04 \text{ (95\% CI)}$$

Identification of Unknown Acid

Based on the experimentally determined molar mass (147 g mol^{-1}) and pK_a (3.50), the unknown acid was identified as **mandelic acid** ($\text{C}_8\text{H}_8\text{O}_3$). Literature values: MW = $152.15 \text{ g mol}^{-1}$ and $\text{pK}_a = 3.41$.

DISCUSSION

Identification and Statistical Analysis

Based on the experimentally determined molar mass of $147 \pm 8 \text{ g mol}^{-1}$ and pK_a of 3.50 ± 0.06 , the unknown acid was identified as mandelic acid ($\text{C}_8\text{H}_8\text{O}_3$). Literature values for mandelic acid are MW = $152.15 \text{ g mol}^{-1}$ and $\text{pK}_a = 3.41$. To determine whether the experimental values agree with the literature values, t-tests were performed at the 95% confidence level.

The t-test compares the experimental mean to the known literature value using:

$$t_{\text{calc}} = \frac{|\bar{x} - \mu|}{s/\sqrt{n}}$$

where $\bar{x}$ is the experimental mean, μ is the literature value, s is the standard deviation, and n is the number of trials. The calculated t-value is compared to the critical t-value of 4.303 for 95% confidence with $n - 1 = 2$ degrees of freedom.

Molar Mass t-test:

$$t_{\text{calc}} = \frac{|147 - 152.15|}{6.08/\sqrt{3}} = \frac{5.15}{3.51} = 1.47$$

Since $t_{\text{calc}} = 1.47 < t_{\text{crit}} = 4.303$, the experimental molar mass agrees with the literature value for mandelic acid at the 95% confidence level.

pK_a t-test:

$$t_{\text{calc}} = \frac{|3.50 - 3.41|}{0.0252/\sqrt{3}} = \frac{0.09}{0.0145} = 6.21$$

Since $t_{\text{calc}} = 6.21 > t_{\text{crit}} = 4.303$, the experimental pK_a does not agree with the literature value at the 95% confidence level. This discrepancy suggests systematic error in the pH measurements or in the determination of the half-equivalence point.

Comparison of Equivalence Point Methods

Two methods were used to determine the equivalence point: the derivative method and the Gran plot method. The derivative method analyzes the first and second derivatives of the titration curve to locate the inflection point, which corresponds to the equivalence point. This method is particularly accurate when sufficient data points are collected near the steep region of the titration curve. The Gran plot method linearizes the pre-equivalence data and extrapolates it to find the x-intercept, which represents the equivalence point.

As shown in Table 2, the derivative method produced equivalence volumes of 30.2, 29.7, and 30.3 mL for the three trials, with excellent agreement within 0.5%. The Gran plot method

yielded values of 29.2, 31.2, and 30.0 mL, showing greater variability between trials. The derivative method is preferred because it utilizes data from the steepest part of the curve, where changes are most dramatic and easily measured, while the Gran plot relies on extrapolation of pre-equivalence data, which can be more sensitive to early data point irregularities and baseline drift.

Sources of Error

Several sources of systematic and random error may have contributed to the discrepancy in the pK_a value. First, carbon dioxide contamination from the atmosphere could have dissolved in the basic NaOH solution over time, effectively lowering its concentration and shifting the measured pH values throughout the titration. Although degassed water was used initially, prolonged exposure during the two-week experiment may have introduced carbonic acid interference.

Second, the pH electrode calibration may have drifted between measurements or may not have been perfectly linear across the entire pH range tested. Small calibration errors near pH 3–4 (the buffer region where pK_a was measured) would directly affect the accuracy of the pK_a determination. Additionally, the response time of the pH electrode may have been insufficient to reach true equilibrium at each measurement point, particularly in regions where pH changes rapidly.

Third, the determination of the half-equivalence point required interpolation between measured data points. If data collection was insufficiently dense in the buffer region, the interpolated pH value could deviate from the true pH at exactly half the equivalence volume. Temperature fluctuations in the laboratory could also affect both the pH electrode response and the acid dissociation equilibrium itself because temperature changes the equilibrium and dissociation rates.

The molar mass determination showed bet-

ter agreement with literature values because it relies primarily on volumetric and mass measurements, which are less susceptible to electrochemical and equilibrium issues that affect pH measurements. The good agreement in molar mass supports the identification of mandelic acid despite the pK_a discrepancy.

Quality and Reasonableness of Results

The titration curves obtained (Figure 1) displayed the characteristic sigmoidal shape expected for a monoprotic weak acid, with a clear buffer region, steep equivalence point transition, and basic post-equivalence plateau. The reproducibility of the derivative method results (within 0.5%) demonstrates good experimental technique in volumetric measurements and consistent sample preparation as well as proper titration techniques and data collection.

The experimentally determined molar mass of 147 g mol^{-1} falls within 3.4% of the literature value of $152.15 \text{ g mol}^{-1}$, which is reasonable given the precision limitations of the analytical balance and the small sample sizes used (approximately 0.46 g per trial). The measured pK_a of 3.50 differs from the literature value of 3.41 by 0.09 pH units, representing a 2.6% relative error. While this exceeds the 95% confidence threshold, it remains within a reasonable range for student laboratory measurements using a glass pH electrode.

Future Experiments

To improve the accuracy of the pK_a determination, several modifications could be implemented. First, multiple pH electrodes could be used simultaneously, and their readings averaged to reduce systematic calibration errors. Second, the buffer region of the titration curve could be measured with higher data density (smaller volume increments) to improve the interpolation accuracy at the half-equivalence point. Third, temperature control could be implemented using a water bath to maintain constant tem-

perature throughout the titration, minimizing temperature-dependent shifts in both the electrode response and the acid dissociation constant.

Additionally, alternative methods for determining pK_a could be employed for comparison. Spectrophotometric titration, which monitors absorbance changes rather than pH, would provide an independent measurement free from pH electrode limitations.³ Finally, conducting the entire experiment in a controlled atmosphere with minimal CO_2 exposure would eliminate potential carbonic acid interference, allowing for more rigorous testing of the standardized NaOH concentration stability over time.

REFERENCES

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