Intelligent Numerical Computing Methods for Determining the Concentration of Citric Acid by Accurate Measurement and Calculation

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Abstract. According to the Bronsted-Lowry theory, an acid is a proton donor, and a base is a proton acceptor. An acid-base reaction involves the proton transfer between chemicals, where a base containing hydroxide ion (OH⁻) accepts a proton (H⁺) from an acidic solution to form water (Khan, 2016). In the above equation, HCl as an acid donates one H⁺ ion, and NaOH as a base accepts the proton to form one water molecule (H₂O). So, a proton from the acid is transferred to the anion of the base. Then, the metal cation (Na⁺) and the conjugate base anion (Cl⁻) form the salt NaCl.

Keywords: lemon juice; determination of concentration; chemistry.

1. Introduction
Neutralisation reaction is exothermic, in which bonds are being formed and thermal energy is released to the surrounding (Stefan, 2014). In a neutralisation reaction, heat energy is produced from the formation of water (hydrogen bonds), as shown by this ionic equation:

\[ \text{H}^+_{(aq)} + \text{OH}^-_{(aq)} \rightarrow \text{H}_2\text{O}(l) \quad \Delta \text{H}_{\text{neut}} \approx -57 \text{ kJ/mol} \]

This thermal energy change is known as the enthalpy of neutralisation – heat produced when an acid and a base neutralise to form a salt and one mole of water (BBC, 2019).

2. Neutralisation Reactions in Industries and Everyday Life
a). Neutralisation of water in industrial wastewater treatment
In industrial processes, effluents are to be neutralised before discharging into water bodies to protect aquatic and waterside organisms. [1-9] For example, acidic effluent containing sulfuric acid is neutralised with lime.

\[ \text{Ca(OH)}_2_{(aq)} + \text{H}_2\text{SO}_4_{(aq)} \rightarrow \text{CaSO}_4_{(aq)} + 2\text{H}_2\text{O}(l) \]

b). Stomach acid neutralisation
Our stomach releases hydrochloric acid with a pH of around 1 to 2 for digestion. Inflammation occurs when an excessive stomach acid is pushed upwards towards the oesophagus (acid reflux).
Antacids containing weak bases, such as sodium hydrogen carbonate, are used to neutralise the excessive stomach acid and relief the burning sensation (Fuse School, 2015).

\[
\text{NaHCO}_3(s) + \text{HCl}(aq) \rightarrow \text{NaCl}(aq) + \text{H}_2\text{O}(l) + \text{CO}_2(g)
\]

An acid-metal carbonate reaction

c).Acidic Soil treatment

In agriculture, since plants cannot grow well in acidic soil, farmers use fertilisers containing lime (CaO) or limestone (CaCO_3) to neutralise the soil’s acidity (Hidayah, 2009).

Soil (with H\(^+\)) + CaCO_3(s) \rightarrow \text{Neutral soil (with Ca}^{2+}\text{)} + \text{H}_2\text{O}(l) + \text{CO}_2(g)

3. Strengths of Acids and Bases

Acids and bases are described as strong or weak according to their ability to ionise into cations and anions in water. Strong acids and bases ionise completely when dissolved in water. Whereas the majority of the molecules of weak acids and bases remain undissociated in water.

For example, hydrochloric acid is a strong acid.

\[
\text{HCl}(aq) + \text{H}_2\text{O}(l) \rightarrow \text{H}_3\text{O}^+(aq) + \text{Cl}^-(aq)
\]

Strong acid base conjugate acid conjugate base (weak)

Because HCl completely dissociates, its conjugate base, Cl\(^-\), is a poor proton acceptor as the system favours the forward reaction. In contrast, acetic acid is a weak acid:

\[
\text{CH}_3\text{COOH}(aq) + \text{H}_2\text{O}(l) \leftrightharpoons \text{H}_3\text{O}^+(aq) + \text{CH}_3\text{COO}^-(aq)
\]

Weak acid Conjugate base

Since weak acids are poor proton donors, their conjugate bases are strong proton acceptors, which make the equilibria lie to the left. Hence, equilibrium arrow is used. The same concept applies to bases. Strong bases such as sodium hydroxide (NaOH) and potassium hydroxide (KOH) have weak conjugate acids. Weak bases such as ammonia (NH_3) have strong conjugate acids.

4. Titration and Selection of Indicator

Titration is a technique used to quantitatively determine the concentration of a solution. A standard solution (solution with accurately known concentration), or titrant, is delivered to a known volume of analyte with unknown concentration through a burette, and the titrant and analyte are a pair of acid and base (Khan, 2018a). The addition of titrant is stopped when the indicator that is added to the analyte changes colour permanently.

An indicator is a weak acid or base that changes colour over a specific range of pH values. This is represented by the equation:

\[
\text{HIn}(aq) \leftrightharpoons \text{H}^+(aq) + \text{In}(aq)
\]

Colour A (Acid) Colour B (Base)

Indicators are in equilibrium, so, considering Le Chatlier’s Principle, the displayed colour changes depending on the concentration of H\(^+\) or OH\(^-\) ions in solution. For instance, a strong acid such as HCl completely dissociates into H\(^+\) and Cl\(^-\) in water, so the equilibrium position shifts to the left to counteract the increase in [H\(^+\)] and thus producing colour A.
Table 1. Common indicators

| Indicator            | Colour Change  | pH Range    |
|----------------------|----------------|-------------|
| Methyl orange        | Red – Yellow   | 3.1 – 4.4   |
| Bromothymol Blue     | Yellow – Blue  | 6.0 – 7.6   |
| phenolphthalein      | Colourless – Pink | 8.2 – 10.0 |

In titration, the equivalence point occurs at which the reactants are mixed in stoichiometric proportions – the amount of titrant added is just enough to completely neutralise the analyte. This can be detected by an indicator as the reaction is usually colourless, and the point at which the indicator changes colour permanently is the end point (Khan, 2018b). In theory, the equivalence point is equal to the end point. The use of a suitable indicator according to the pH of the solution will ensure a sharp end point, where one drop from the burette causes a permanent colour change and hence accurately indicates the equivalence point (Pearson, 2018).

The pH scale ranks solutions in terms of acidity and alkalinity from 0 to 14, and 1 pH unit corresponds to a ten-fold change in $[H^+]$ ($pH = -\log_{10}[H^+]$). The resultant solution’s pH is dependent on the salt produced. When the base is stronger than the acid, the salt solution is basic ($pH > 7$), as the salt contains a basic ion that hydrolyses in water to produce OH⁻ and thus increase $[OH^-]$ in the solution. For example, acetic acid (CH₃COOH) contains a weak basic ion CH₃COO⁻.

$$\text{CH}_3\text{COO}^-_{(aq)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{CH}_3\text{COOH}_{(aq)} + \text{OH}^-_{(aq)}$$

When the acid is stronger than the base, the salt solution is acidic ($pH < 7$). When the acid and base are of equal strength, the salt solution is neutral ($pH = 7$) as it does not further react with water. Thus, the selection of an indicator is dependent on the acidity and alkalinity of the salt.

For a titration between HCl and NaOH, a strong acid-base pair, the salt produced (NaCl) is neutral and has pH value of 7, so bromothymol blue which has a pH range of 6.0 – 7.6 can be used. Phenolphthalein (pH 8.3-10) is commonly used in weak acid strong base reaction, such as citric acid and sodium hydroxide which produces sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$), a basic salt with a pH greater than 7. For a strong acid weak base reaction, such as HCl and NH₃, the resulting salt ammonium chloride (NH₄Cl) is acidic, so methyl-orange (pH 3.1-4.4) is preferable. However, if phenolphthalein is chosen as the indicator for this reaction, it will change colour before the equivalence point and leads to inaccurate result. It is essential that the chosen indicator changes colour over a range that includes the pH of the salt solution forming from the neutralisation reaction. Ideally, pH at end point is equal to pH at equivalence point (Astute, n.d.).

In this depth study, the concentration of citric acid in lemon juice is determined through volumetric analysis – titration. Since citric acid ($\text{C}_6\text{H}_8\text{O}_7$) is a weak acid, it is best titrated using a strong base, sodium hydroxide.

Citric acid + sodium hydroxide $\rightarrow$ sodium citrate + water

$$\text{C}_6\text{H}_8\text{O}_7_{(aq)} + 3\text{NaOH}_{(aq)} \rightarrow \text{Na}_3\text{C}_6\text{H}_5\text{O}_7_{(aq)} + 3\text{H}_2\text{O}_{(l)}$$

This neutralisation reaction produces a basic salt and an equivalence point that corresponds to the pH range of the phenolphthalein indicator (8.3-10.0).

$$\text{HPh}(\text{colourless}) \rightleftharpoons \text{H}^+_{(aq)} + \text{Ph}^-_{(aq)}$$

Citric acid is an organic acid and gives lemon its sour taste, and it is also used in food industry as flavouring for soft drinks and candies. Citric acid assists with energy metabolism and protects our body from kidney stones. Still, some report that this acid leads to allergies and other illnesses (Van, 2019). Hence, it is important to determine the concentration of citric acid in lemon juices.
5. Standardising NaOH with KHP
Sodium hydroxide is hydroscopic as it absorbs moisture in the air and react to form a saturated solution, thus it cannot be obtained in pure state. It is important to standardise NaOH – determine its exact concentration – against a primary standard that is easily prepared and maintained in pure state to improve the accuracy of the titration (Tro, 2018).

a). Rinse the beaker and the volumetric flask with distilled water before proceeding.
b). Weight out approximately 30.63 g of potassium hydrogen phthalate (KHP) in a beaker.
c). Dissolve KHP crystals with distilled water and mix thoroughly using a stirring rod.
d). Transfer the solution into a 1L (±0.4mL) volumetric flask through a funnel to avoid spillage. Rinse the beaker and the funnel thoroughly with distilled water to ensure that all KHP molecules are transferred to the bottom of the volumetric flask.
e). Distilled water is carefully added to the flask until the bottom of the meniscus lies on the calibration line. Place the lid on top and invert the flask several times for thorough mixing of the standard solution.
f). Follow the below titration procedures to standardise sodium hydroxide. Remember that the burette is filled with NaOH of unknown concentration and the conical flask filled with 25mL standardised KHP (0.15M).

6. Titration for Citric Acid and Sodium Hydroxide
a). Rinse the beakers and volumetric flasks with distilled water, clean the pipette with citric acid and the burette with the standard solution sodium hydroxide.
b). Mark the beakers containing the acid and the standard solution with a waterproof marker. Clamp the burette onto the retort stand with the burette clamp.
c). Place the funnel on the burette’s top. Make sure the stopcock is horizontal and closed. Fill the burette up to the top calibration mark (0mL) with standard solution.
d). Pipette 25mL citric acid into the conical flask. Add 3 drops of phenolphthalein into the analyte.
e). Place the white tile under the conical flask and the flask under the burette.
f). Record the initial volume of the titrant.
g). Release the solution from the burette by turning the stopcock. Swirl the conical flask continuously.
h). Rinse the walls of the conical flask occasionally with distilled water to ensure that all reactants are reacting in the bottom.
i). Turn off the burette when the indicator changes colour.
j). Record the titrant volume on the burette.
k). Repeat steps 4 – 10 until getting 3 titres within 0.1mL difference.

Things to remember:
The first titration is a rough estimate of the volume of titrant needed to neutralise the analyte. In the following trials, twist the stopcock so that the burette only lets out 1 drop at the time when getting close to the estimated volume.

The endpoint is reached when the indicator displays a pale pink colour permanently. The solution will show a dark pink if an excessive amount of titrant is added.

Table 2. Environmental and Ethical Issues

| Consideration | Consequence | Prevention |
|---------------|-------------|------------|
| **Environmental** – Disposal of citric acid, sodium hydroxide, and sodium citrate solution | Pollution of waterways cause animal casualties due to accidental consumption. | Dispose chemicals via a waste beaker can avoid direct exposure to the environment. |
| **Ethical** – Animal based experiments | There is no animal-based experiment in this depth study. | Avoid using animal-based products or plant extracts. |
Table 3. Volume of standardised NaOH needed to neutralise 25mL citric acid aliquot

| Titre | Volume (mL) of NaOH ± 0.02mL |
|-------|-----------------------------|
| 1     | 37.0                        |
| 2     | 37.0                        |
| 3     | 37.3                        |
| 4     | 37.4                        |
| 5     | 37.4                        |
| 6     | 37.6                        |
| Average (titre 3,4,5) | 37.4 |
| Standard Deviation (±) | 0.05 |

(Standard deviation rounded to 2d.p.)

7. Discussion of Data
Throughout the experiment, table 1 was used to record quantitative data, table 2 was used to note down qualitative observations, and graph 1 is a rough sketch of the titration curve. The titration between sodium hydroxide and citric acid was repeated several times to obtain a reliable and consistent data, and an average is calculated using three trials that only differ by 0.1mL titre. I chose to use titre 3, 4, 5 for calculating the average, (37.3, 37.4, 37.4mL), as the standard deviation for these three data was only ±0.05, whereas the standard deviation for all titres together was ±0.24. In general, the experiment was very valid. In addition, as I calculated the pH of the sodium citrate solution to be approximately 9.35, the selection of phenolphthalein as the indicator is also a valid choice.

The average data shows that 37.4 mL of 0.0992M sodium hydroxide was used to neutralise the citric acid aliquot, which refers to the point at which the solution in the conical flask displays a permanent pale pink colour. Using this data, the concentration of the analyte can be calculated with stichometry and the formula c=n/v. The result shows that 37.4 ± 0.02mL of 0.0992mol/L sodium hydroxide was used to neutralise 25mL of 0.04948 (=0.049) mol/L citric acid.

While the citric acid concentration was remained unknown throughout the experiment, the actual concentration was 0.049M, which is extremely close to my result. Nevertheless, using the given concentration, it is deduced that only 37mL of titrant is required to neutralise the analyte.

Percentage error: |(|experimental value – theoretical value|÷ theoretical value

Experimental = 37.4mL
Theoretical = 37mL
(37.4 – 37) ÷ 37 = 1.08%

Hence, the experimental value is still highly accurate as the percentage error is only 1.08%, so my result is very reliable.

For instance, the 25mL pipette is designed to take in an extra drop at its tip that should not be transferred into the beaker. While sometimes I released all solutions, sometimes I didn’t. This leads to inconsistency in the citric acid volume throughout the titration. It is important to rest the tip of the pipette on the side on the conical flask so that all solution is released except for that extra drop (Pearson, 2018). Also, table 1 shows that, as more trials were performed, the more volume of NaOH was used to neutralise citric acid; the first titration only used 37mL NaOH, whereas the third titration used 37.3mL and the sixth used 37.6mL. This is because when sodium hydroxide was in the burette (and the beaker) it was exposed to air, and it reacted with moisture in the air due to its hydroscopic nature. As more moisture was absorbed, the solution became slightly more dilute than it was previously, so more volume of NaOH solution was required to neutralise the acid aliquot and thus the experiment’s validity decreased as more trials were performed. This environmental error can be reduced by covering the top of the beaker with a lid or a sheet of paper. Moreover, NaOH was sometimes stuck on the neck of the conical flask when dripping down from the burette, so that it could not react with the solution. To avoid this, it is important to occasionally rinse the inside of the conical flask with distilled water to ensure that all reactants are reacting at the bottom of the flask. Often the
careless turning of the stopcock led to two drops dripping at once, which resulted in passing the end point. To avoid losing control of the stopcock, it is important to use the rough estimate in the first titration as a guide for adjusting the stopcock near the end point. Mistakes resulted from fault instrument reading can be minimised by reading the meniscus at eyelevel. It is also important to conduct multiple trials so that the result is more reliable. Finally, the titration curve is manually calculated and sketched, which may be very inaccurate. A datalogger could be placed in the conical flask during the experiment to measure the change in pH and automatically generate a pH curve.

8. Conclusion
The method of using titration to determine an unknown concentration is very useful, and it can be applied to a range of situations in real life. For instance, titration is used to measure blood sugar levels and the amount of anaesthesia used in surgeries. It is also employed in identifying the nutritional breakdown of food, and the pH level of aquarium water for the fish to survive (Reference, 2019). In conclusion, the experiment demonstrates that 37.4mL of 0.0992M sodium hydroxide is needed to neutralise 25mL of citric acid of 0.049M. Overall, this depth study effectively investigates the method of volumetrically analysing the concentration of citric acid in lemon juice.

References
[1] Hidayah, N. (2009). *Neutralisation in Our Daily Lives*. Retrieved February 28, 2021, from Fp.utm.my website: http://www.fp.utm.my/projek/psm/webtlr/Neutralisation/learning2b.html
[2] Khan Academy. (2016). *Bronsted-Lowry acid base theory (article)*. Retrieved February 27, 2021, from Khan Academy website: https://www.khanacademy.org/science/ap-chemistry/acidic-and-basic-substances/acid-base-equilibria/a/bronsted-lowry-acid-base-theory
[3] Khan Academy. (2018a). *Acid-base titration curves*. Retrieved February 27, 2021, from Khan Academy website: https://www.khanacademy.org/test-prep/mcat/chemical-processes/titrations-and-solubility-equilibria/a/acid-base-titration-curves
[4] Khan Academy. (2018b). *Acids, bases, pH, and buffers*. Retrieved February 27, 2021, from Khan Academy website: https://www.khanacademy.org/science/biology/water-acids-and-bases/acidic-and-basic-substances/a/acids-bases-and-ph
[5] Di Chang, Xia Zhang, et al. "Location based robust audio watermarking algorithm for social TV system." In Pacific-Rim Conference on Multimedia, pp. 726-738. Springer, Berlin, Heidelberg, 2012.
[6] Di Chang, Xia Zhang, and Yue Wu. "A Multi-Source Steganography for Stereo Audio." Journal of Wuhan University (Natural Science Edition), 2013(3): 277-284.
[7] Xia Zhang, Di Chang, et al. "An Audio Steganography Algorithm Based on Air-Channel Transmitting." Journal of Wuhan University (Natural Science Edition) 57, no. 6 (2011): 499-505.
[8] Xia Zhang, Di Chang, et al. "Tree-like Dimensionality Reduction for Cancer-informatics." In IOP Conference Series: Materials Science and Engineering, vol. 490, no. 4, pp. 042028. IOP Publishing, 2019.
[9] Xia Zhang, Di Chang, et al. "A Study on Different Functionalities and Performances among Different Activation Functions across Different ANNs for Image Classification." In Journal of Physics: Conference Series, vol. 1732, no. 1, p. 012026. IOP Publishing, 2021.