

Titration via acid-base neutralisation

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List of abbreviations, constants and variables:

Abbreviation	Definition
HCl	Hydrogen chloride/hydrochloric acid
NaOH	Sodium hydroxide
NaCl	Sodium chloride
H ₂ O	Water
(aq)	Aqueous
dm	Decimetre
Cl ⁻	Chloride ion
H ₃ O ⁺	Hydronium ion
H ⁺	Hydrogen ion/proton
OH ⁻	Hydroxide ion
OME	Ordnance Munitions and Explosives
RDX	Hexogen
PETN	Pentaerythritol tetranitrate
TNT	Trinitrotoluene
DCM	Dichloromethane

List of constants and variables:

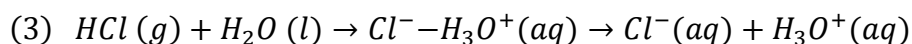
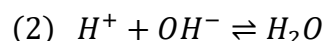
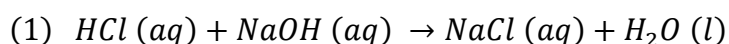
Abbreviation	Definition
V	Volume measured in mL or L
V _{NaOH}	Volume of NaOH needed for neutralisation measured in mL
V _{final}	Final volume reading of burette measured in mL
V _{initial}	Initial volume reading of burette measured in mL
C _{NaOH}	Concentration of NaOH measured in mol dm ⁻³
n _{NaOH}	Amount of NaOH measured in mol

n_{HCl}	Amount of HCl measured in mol
C_{HCl}	Concentration of HCl measured in mol dm ⁻³
V_{HCl}	Volume of HCl measured in mL
$\bar{x}$	Arithmetic mean
N	Number of values in a dataset for an arithmetic mean
x_i	Numbered entry in a data set where i exists in a defined range
Z, X, Y	Quantities in an error calculation
$\Delta z, \Delta x, \Delta y$	Errors in quantities in an error calculation

Introduction

Titration a common laboratory technique typically used to determine the concentration of a solution by mixing it with another solution of known concentration called a standard solution. It can therefore be hypothesised that when given a known volume of hydrochloric acid (HCl) with an unknown concentration, a standard solution of sodium hydroxide (NaOH) can be used in combination with the indicator phenolphthalein to identify the neutralisation point. Furthermore, it could be hypothesised that the concentration of a sample of HCl could be determined from the results of such a titration. Phenolphthalein is colourless in acidic solutions and pink in basic solutions, so a transition from colourless to faint pink would indicate the solution has just passed the neutralisation point. As such, the independent variable in this experiment is the volume of the standard solution added, and the independent variable is the colour of the solution.

The neutralisation reaction of HCl and NaOH can be written as seen in [eq. 1]. While neutralisation reactions are typically depicted as a reaction between hydrogen ions (H⁺) and hydroxide ions (OH⁻) [eq.2], this is somewhat inaccurate. When HCl enters an aqueous solution, water (H₂O) molecules engage in a complex interaction to form a contact ion pair of chloride [eq. 3] and hydronium (H₃O⁺), which is then broken apart into individually solvated ions [1]. This hydronium ion is what protonates the hydroxide ion in a neutralisation reaction.



At the point of neutralisation, the amount of NaOH added into the mixture must be stoichiometrically equivalent to the amount of HCl which was initially present in the sample. The volume of NaOH solution added can be measured using a precise and accurate piece of equipment like a burette and volumes can be converted to the more conventional units of litres or cubic decimetres (dm³) [eq. 4] for later calculations if necessary. Using this, the volume necessary for neutralisation (V_{NaOH}) can be found via [eq. 5].

$$(4) \quad V(\text{in L or dm}^{-3}) = \frac{V(\text{in mL or cm}^{-3})}{1000}$$

$$(5) \quad V_{\text{NaOH}} = V_{\text{final}} - V_{\text{initial}}$$

The known concentration of the standard solution (C_{NaOH} , which is $0.09977 \text{ mol dm}^{-3}$ in this experiment) can then be used to calculate the amount of NaOH added in moles (n_{NaOH}) [eq. 6]. Since this is equivalent to the number of moles of HCl (n_{HCl}), the concentration of the sample of HCl (C_{HCl}) can be determined [eq. 7].

$$(6) \quad n_{\text{NaOH}} = V_{\text{NaOH}} \times C_{\text{NaOH}}$$

$$(7) \quad C_{\text{HCl}} = \frac{n_{\text{HCl}}}{V_{\text{HCl}}}$$

Results

After performing 3 titrations the relevant physical quantities of volume, amount of substance and concentration mentioned above were then calculated and tabulated, see [table 1]. It should be noted that although some quantities have been rounded to the appropriate significant figures, the full values were used for all calculations. From the original iteration data, it cannot immediately be observed that in iterations 1 and 2 V_{NaOH} are concordant within 0.1 mL, however the V_{NaOH} was normalised to conform to the 25.0 mL of HCl standard, suggesting that it would have been 16.6 mL if prepared correctly, and therefore within 0.1 mL of 16.5. The original volume of 23.2 mL was used in all calculations.

Iteration	V_{HCl} (mL)	V_{initial} (mL)	V_{final} (mL)	V_{NaOH} (mL)	C_{NaOH} (mol dm^{-3})	$n_{\text{HCl}}/n_{\text{NaOH}}$ (mol)	C_{HCl} (mol dm^{-3})
Rough	25.0	0.0	17.0	17.0	0.09977	0.00170	0.0678
1	25.0	0.0	16.5	16.5	0.09977	0.00165	0.0658
2	35.0	13.0	36.2	23.2	0.09977	0.00231	0.0661
2 (Normalised)	25.0	n/a	n/a	16.6	n/a	n/a	n/a
						Average C_{HCl} (mol dm^{-3})	0.0660

Table 1: Observed and derived quantities describing the two solutions

Using the concentrations of iterations 1 and 2, calculated to be $0.0658 \text{ mol dm}^{-3}$ and $0.661 \text{ mol dm}^{-3}$ respectively, an arithmetic mean average ($\bar{x}$) [eq. 8] was calculated to be $0.660 \text{ mol dm}^{-3}$.

$$(8) \quad \bar{x} = \frac{1}{N} \sum_{i=1}^N x_i$$

This data was additionally plotted as a bar chart to easily compare for concordance as seen in [fig. 1]. Furthermore, the resultant concentrations of HCl were plotted alongside the calculated average in [fig.2].

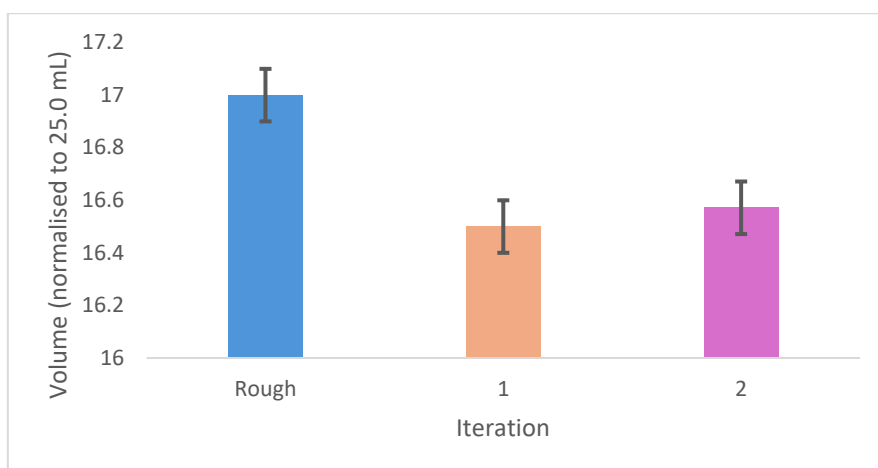


Figure 1: The volumes of neutralisations for each of the three iterations with error bars, 1 and 2 within 0.1 mL of each other.

Additionally absolute and relative errors were calculated and tabulated [table 2] for the volumes of HCl and NaOH, as well as the concentration of HCl. These were included in [fig. 1, 2] as error bars. Further details of error calculation and propagation can be found in the discussion below.

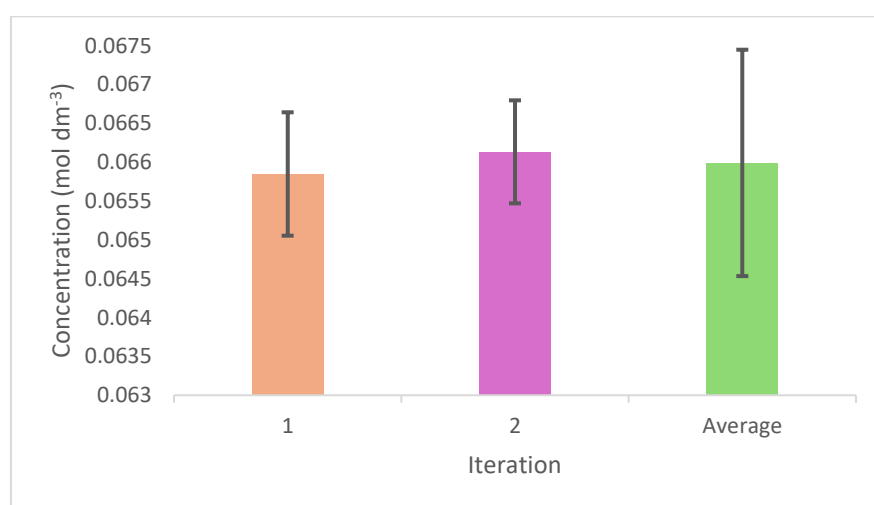


Figure 2: Comparison of concentrations

Discussion

Error analysis

From the results mentioned previously [table 1] it can be surmised that the first hypothesis has been confirmed, since the neutralisation point was recorded in each of the three iterations. The second hypothesis raised in this experiment was the determination of the initial HCl concentration. It can be reasonably concluded that this hypothesis was also confirmed by the calculation of two concentrations from concordant volumes, followed by the

calculation of an average. This combined with the measurement error propagation in [table 2] suggests that the true value of the original concentration of HCl is highly likely to be in the range depicted in [fig. 2].

Iteration	V _{HCl} Absolute error (mL)	V _{HCl} Relative error %	V _{NaOH} Absolute error (mL)	V _{NaOH} Relative error %	C _{HCl} Absolute error (mol dm ⁻³)	C _{HCl} Relative error %
Rough	±0.15	0.6	±0.1	0.590	±0.000806	1.19
1	±0.15	0.6	±0.1	0.606	±0.000794	1.21
2	±0.2	0.571	±0.1	0.431	±0.000663	1.00
Average					±0.00146	2.21

Table 2: Measurement errors and their propagation into calculated values

The measurement errors in this experiment were only propagated via basic error calculations [eq. 9, 10, 11], however, more sophisticated error propagation techniques exist and could be used in future titrations to give more confidence in the range of calculated concentrations.

$$(9) \text{ if } Z \pm \Delta z = X \pm x + Y \pm y, \quad \Delta z = \Delta x + \Delta y$$

$$(10) \text{ if } Z \pm \Delta z = X \pm x \times Y \pm \Delta y, \quad \frac{\Delta z}{Z} = \frac{\Delta x}{X} + \frac{\Delta y}{Y}$$

$$(11) \text{ relative error (\%)} = \frac{\Delta z}{Z} \times 100$$

In addition to measurement errors, several other potential sources of uncertainty were present. These include glassware parallax error, glassware levelness, loss of reactants, poor tap control, late colour change identification, and NaOH solution concentration.

Effort was made to ensure all glassware measurements were made level with the meniscus, so the uncertainty associated with this is likely negligible. On the other hand, most measurements were made using handheld glassware and the clamp stands used with the burette were adjust by hand also. While this error is likely minor as well, future work could be done using a spirit or digital level to ensure measurement reading accuracy.

Loss of reactants is an avenue for error typically characterised by the unwanted deposition of reactants into non-reacting environments, or the introduction of unwanted reactive species into a reagent. There are three main ways this could have occurred in this experiment. The first was droplet deposition on the upper parts of the conical flask. If this occurred, trace amounts of HCl may have been left on the upper parts of the flask, meaning they could not have reacted with the NaOH in solution. This is likely negligible however due to the overhanging walls of the flask promoting downward motion of fluids on its surface, as well as the care taken to prevent this from occurring. The second possible reason for reactant loss

was glassware contamination. Trace amounts of unknown compounds in any of the pieces of glassware could affect the results, not only by reacting with the solutions present within them, but also by changing the overall concentration of the solution. Although care was taken to wash the glassware with appropriate solutions, glassware can be difficult to clean thoroughly without leaving residue. The third possible cause of reactant loss was the water pH. Since the natural pH range of water can vary based on location, it was possible that the water was slightly more basic or acid than pH 7. This could have skewed the volume necessary for neutralisation in either direction. To avoid this in future work, the pH of the water should be tested.

The human error associated with poor tap control and late colour identification were of great concern so significant effort was taken to ensure dropwise addition near to the suspected neutralisation point, alongside the use of long wait times between addition, vigorous swirling and the introduction of a white tile to aid in colour identification.

The last source of uncertainty was the concentration of NaOH solution. The given concentration is assumed to be accurate to exactly four significant figures, and as such any derived unit can only be at least 4 significant figures long.

Ordnance, Munitions and Explosives (OME) applications

Titration is a widely used technique in the field of volumetric analysis, and such analysis is particularly important in the OME industry which is innately hazardous. This is because, when working with energetic compounds, knowing the exact amount of such a compound is required to calculate the energy a given sample will produce. Hence volumetric techniques like titration are frequently employed to quantify the purity [2], quantity [3] and stability [4] of energetic compounds. Titration also has applications in explosive substance detection [6].

Research into the insensitive high-explosive FOX-7 [2], more formally known as 1,1-diamino-2,2-dinitroethene, used titration to assay its purity. The FOX-7 was titrated in a solution of N,N-dimethylformamide against the base sodium methoxide dissolved in an organic mixture of benzene and methanol. This was possible due to the weak acidity of FOX-7, allowing for an acid-base reaction. Azo violet was used as an indicator, with a colour change from red to blue showing the equivalence point. It stands to reason that titration could be used to assay many other explosive/energetic compounds in a similar manor. This may be because most explosive compounds contain nitro groups, which are electron withdrawing. This can draw electron density away from potential electron pair acceptors, making compounds with nitro groups potential Lewis acids.

In fact, this is exactly what D. Sarson [3] showed in 1958 when several commonly used explosives and oxidisers were able to be titrated in non-aqueous solutions to determine quantity. Oxidisers like sodium nitrate and ammonium nitrate were titrated as bases in an acetic acid and chloroform solution, while explosives such as trinitrotoluene (TNT), hexogen

(RDX) and pentaerythritol tetranitrate (PETN) were titrated as acids in dimethylformamide alongside various other organic compounds.

Meyer et al. [4] noted that the stability of nitrocellulose could be heated to 132°C for 2 hours, then extracted with water and filtered for nitrous oxides which could then be quantified via titration with special apparatus. It is stated that Siebert also suggested improvements upon this method such as using hydrogen peroxide instead of water. These methods are still used in the OME industry and in fact are listed as standard tests for nitrocellulose stability in the North Atlantic Treaty Organisation standards for nitrocellulose [5].

A sensitive black powder detection technique was laid out by Liang et al. [6] in which titration is performed by their ion mobility spectrometer with sulfur ions, superoxide ions and dichloromethane (DCM). This integration with other spectroscopic techniques as part of a wider piece of machinery is a novel approach to explosive detection which could be of great interest to the OME industry.

Conclusion

In summary, the two hypotheses were tested and proven with the HCl solution being successfully titrated to the neutralisation point and the HCl concentration being calculated with a defined range of uncertainty. While several possible sources of error did exist, many were addressed via the methodology and suggestions were made for future research to avoid such uncertainties, such as use of level determining equipment and water pH determination. Applications of titration in the OME industry were explored, and it was found that titration is frequently used for quantitative analysis of energetic compounds.

References

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- [5] North Atlantic Treaty Organisation, "STANAG/AOP-4178," Feb. 2017.
- [6] X. Liang et al., "Sensitive Detection of Black Powder by a Stand-Alone Ion Mobility Spectrometer with an Embedded Titration Region," *Analytical Chemistry*, vol. 85, no. 10, pp. 4849–4852, Apr. 2013, doi: <https://doi.org/10.1021/ac400337s>.

Appendix

Method:

1. Before titration, each piece of glassware was washed thrice with a small quantity of the solution they were going to be used to measure.
2. Three solutions of the unknown sample of HCl (25.0 mL) diluted with water (10.0 mL) were prepared in conical flasks by measuring with a graduated pipette and measuring cylinder respectively and then ejecting the contents into each conical flask. The third solution was prepared using excess HCl (35.0 mL).
3. A burette was filled with NaOH solution (50.0 mL, 4.99 mmol).
4. The first prepared mixture was used to gauge an approximate titre via the rapid addition of sodium hydroxide while swirling the prepared mixture. The meniscus level was noted when the mixture turned pink.
5. The burette was then refilled.
6. NaOH solution was added rapidly until approaching the noted volume. Upon reaching the noted volume the NaOH solution was added dropwise with vigorous swirling until the mixture remained faintly pink after prolonged observation and agitation.
7. Step 6 was reiterated until concordant results were observed.

$$13 + 16 = 29$$

DATA SHEET to RECORD OBSERVATIONS, CALCULATIONS and RESULTS

STUDENT'S NAME: Cyno
 PARTNERS' NAMES: Callum

REPORT IS DUE MARCH 21, 2025 @ 3.00 pm submitted via Moodle

(DD: March 28, 2025 @ 3.00 pm)

TITRATION DATA SHEET

Molarity of the standard base solution: $M_{\text{NaOH}} = 0.09977 \text{ mol dm}^{-3}$

$c = \frac{n}{v}$

FLASK	1 rough titration	2	3	4
V_{HCl} (mL) from pipette	25.6	25.0	~~25.0~~	25.0
Initial burette reading	0	0	~~13.0~~	13.0
Final burette reading	~~18.00~~	16.50	~~36.42~~	36.20
V_{NaOH} (mL)		16.50		23.2
Moles of NaOH		1.64×10^{-3}		2.315×10^{-3}
Moles of HCl		"		"
Molarity of HCl		0.0658	0.0661	

$$\begin{array}{r} 30 \ 9 \\ 4 \ 120 \ 12 \\ \hline 182 \end{array}$$

$$3.3 \times 4$$

$$\begin{array}{r} 16.5 \\ 5 \\ \hline \end{array}$$

$$0.07$$

$$16.5$$

Precision and Accuracy

You should record pipette and burette readings to the nearest 0.05 cm^3 (approximately one drop). Consecutive titrations should agree to within 0.10 cm^3 and, you should repeat the titration until this is achieved.