

Unit 3 Chemistry - Volumetric Analysis

Volumetric analysis is a quantitative chemical analysis used to determine the unknown concentration of one reactant [the analyte] by measuring the volume of another reactant of known concentration [the titrant] needed to completely react with the first. The volumetric analysis is also known as a titration.

Glossary of Terms – Volumetric Analysis [Titration]

Pipette	a calibrated tube or pump device that can deliver an accurate set volume of liquid sample containing the analyte [reactant of unknown concentration]
Aliquot	the set volume of sample delivered by a pipette eg. 25.00 ml
Burette	a calibrated tube fitted with a tap that can be used to deliver a measurable volume of titrant into the reaction flask containing the aliquot of sample.
Titrant	the reactant of exactly known concentration that is delivered by the burette
Indicator	substance that is added to the reaction vessel to indicate [usually by colour change] that the titrant has just reached excess. Some titrations don't involve an indicator, the end points being self indicating or indicated by an instrument such as a pH meter
Endpoint	the point at which the burette tap is closed and titration is stopped, usually in response to an indicator changing colour
Equivalence point	the point at which exactly the right number of moles of titrant reactant, according to stoichiometry, have been added to the analyte to complete the reaction
Titre	the measured volume of titrant delivered from the burette to reach the endpoint of the titration

A typical Titration:

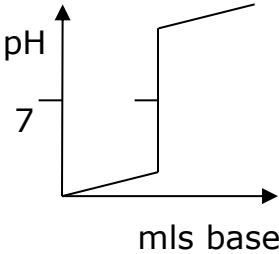
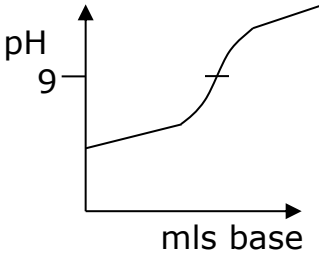
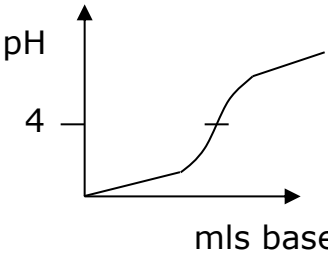
To determine the % ethanoic acid [CH_3COOH] content of vinegar, the acid in a certain amount of vinegar is reacted with a measured amount of standard $\text{NaOH}_{(\text{aq})}$ solution, using an indicator that changes colour to signal the end of the reaction.

In a typical titration ...

- a 25.00 ml **aliquot** of vinegar is **pipetted** into a 250 ml conical flask
- 5 drops of phenolphthalein **indicator** added.
- a **burette** is rinsed and filled with standard 0.100 M sodium hydroxide solution
- an initial burette reading is taken
- the burette tap is opened, the $\text{NaOH}_{(\text{aq})}$ **titrant** is added to the swirled flask, quickly at first, then slowly as the **endpoint** looms
- on adding a single drop, the indicator changes colour and the titration is stopped
- a final burette reading is taken and the **titre** determined
- a balanced equation and stoichiometry is used to calculate the % ethanoic acid

Indicators

- an indicator is used to identify the equivalence point in a titration reaction, with a change in colour signalling when the titration should be stopped
- for acid/base titrations the indicator must change colour at a pH found at the equivalence point ...

 <p>strong acid + strong base sharp end point at pH = 7</p>	 <p>weak acid + strong base broad endpoint at pH \approx 9</p>	 <p>strong acid + weak base broad endpoint at pH \approx 4</p>
Bromothymol blue indic. changes at pH \approx 7.0	Phenolphthalein indicator changes at pH \approx 8.5	Methyl orange indicator changes at pH \approx 4

Standardising Titrants

- the reliability of a volumetric analysis relies heavily on the accurately known concentration of one of the reactants, usually the titrant
- if the known solution is not a **primary standard**, it should be standardised by reacting it with a primary standard substance.
- Primary standard substances must be **very pure**, have a **known formula**, be **easily dried** and soluble, be **relatively stable** in solution and have a **high molar mass** [to reduce weighing uncertainty]
- Examples of primary standard substances include ... **sodium carbonate** [Na_2CO_3], used to standardise acid solutions; **potassium hydrogen phthalate** [$\text{KH}(\text{C}_8\text{H}_4\text{O}_4)$], used to standardise bases;

Measurement Uncertainties of Volumetric Glassware

- the glassware used in volumetric analysis has uncertainties associated with the volumes measured and these must be considered when calculating

20 mL pipette = 20.00 \pm 0.05 mL	250.0 mL vol. flask = 250.0 \pm 0.3 mL
50 mL burette = \pm 0.02 mL per reading \rightarrow titre = \pm 0.04 mL	

- in calculations, the answer should be given in the least number of significant figures associated with measurements used to calculate it

Concordant Titres

- to minimise random errors, titrations are repeated until **concordant** titres are obtained; titres are considered concordant if they differ by no more than 0.10 mL
- the titre used in calculations will be the **average of concordant titres**

Example of Volumetric Analysis #1 [acid/base titration]

The % Ethanoic Acid in Vinegar

The amount of ethanoic acid in vinegar can be determined by volumetric analysis. Being an acid, it will react with sodium hydroxide, a base, to produce a salt and water... $\text{CH}_3\text{COOH}_{(\text{aq})} + \text{NaOH}_{(\text{aq})} \rightarrow \text{NaOOCCH}_3_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})}$

The endpoint of an acid-base titration can be shown by using an indicator dye that changes colour at a pH close to the equivalence point. A pH meter could also be used to detect the equivalence point.

The Titration:

- a 10.00 ml aliquot of the vinegar sample is pipetted into a conical flask
- 3 drops of colourless phenolphthalein indicator are added to the flask
- a burette is rinsed and filled with standard 0.0560 M $\text{NaOH}_{(\text{aq})}$ titrant
- the initial burette reading is recorded as 0.65 ml
- the titration begins, with titrant being added to swirled reaction flask
- as the pink colour in the flask becomes slower to disappear, the titration is slowed to a dropwise addition of titrant
- on addition of a single final drop, a permanent pink colour persists and the titration is stopped at the endpoint.
- the final burette reading is 17.35 ml \therefore titre = $17.35 - 0.65 = 16.70$ ml
- the process is repeated and a titre of 16.75 ml obtained.

The Calculation:

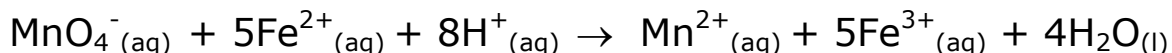
- balanced equation = $\text{CH}_3\text{COOH}_{(\text{aq})} + \text{NaOH}_{(\text{aq})} \rightarrow \text{NaOOCCH}_3_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})}$
mol ratio = 1 : 1
- average titre = $[16.70 + 16.75]/2 = 16.725$ ml = 0.016725 L
- amount of NaOH titrant **n = CV** = $0.0560(0.016725) = 9.366 \times 10^{-4}$ mole
- amount of CH_3COOH in 10 ml sample = 9.366×10^{-4} mole [1:1 mole ratio]
- mass of CH_3COOH in sample = **nM_r** = $9.366 \times 10^{-4}(60.0) = 0.056196$ g
- % [w/v] ethanoic acid in vinegar = $[0.056196/10.00] \times 100 \approx 0.562\%$

Note: % [w/v] means "mass of substance per 100 ml of liquid sample"

Example of Volumetric Analysis #2 [redox titration]

The % Iron in a Rock Sample

The amount of iron in a crushed rock sample is determined by volumetric analysis. The sample will be dissolved in sulfuric acid and the $\text{Fe}^{2+}_{(\text{aq})}$ ions in the solution reacted with potassium permanganate [$\text{KMnO}_{4(\text{aq})}$] solution, an intensely purple, strong oxidant ...



In this redox reaction ...

- the $\text{Fe}^{2+}_{(\text{aq})}$ ions are oxidised to $\text{Fe}^{3+}_{(\text{aq})}$ ions
- the $\text{MnO}_4^{-}(\text{aq})$ ions are reduced to $\text{Mn}^{2+}_{(\text{aq})}$

The titration is self indicating because the permanganate ions [$\text{MnO}_4^{-}(\text{aq})$] are an intense purple colour and any excess of them in the reaction flask would be an immediately obvious signal to stop the titration.

The Titration:

- duplicate 20.00 g samples of rock are weighed into conical flasks
- the samples are dissolved in a sulfuric acid solution
- the samples are then titrated with 0.125 M $\text{KMnO}_{4(\text{aq})}$ solution until the first permanent purple colour persists in the flask
- an average titre of 20.35 ml of 0.125 M $\text{KMnO}_{4(\text{aq})}$ titrant is obtained

The Calculation:

- equation = $\text{MnO}_4^{-}(\text{aq}) + 5\text{Fe}^{2+}(\text{aq}) + 8\text{H}^{+}(\text{aq}) \rightarrow \text{Mn}^{2+}(\text{aq}) + 5\text{Fe}^{3+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$
mol ratio = 1 : 5
- amt. of $\text{MnO}_4^{-}(\text{aq})$ titrant **n = CV** = $0.125(0.02035) = 2.54375 \times 10^{-3}$ mole
- amt. of $\text{Fe}^{2+}_{(\text{aq})}$ in 20 g sample = $5(2.54375 \times 10^{-3})$ mole [1:5 mole ratio]
= 0.0127185 mole
- mass of Fe in 20.00 g sample = **nMr** = $0.0127185(55.85) = 0.710328$ g
- % [w/w] Fe in rock sample = $[0.710328/20.00] \times 100 \approx 3.55$ %

Note: %[w/w] means "mass of substance per 100 g of weighed sample"

Example of Volumetric Analysis #3 [diluted sample]

The % w/w Salt in a Biscuit

The salt [NaCl] content in a biscuit is determined by volumetric analysis, after the salt in the biscuit is dissolved in distilled water and diluted to an exact volume in a volumetric flask. Aliquots of the diluted sample are then reacted with silver nitrate solution [$\text{AgNO}_{3(\text{aq})}$], forming a precipitate of silver chloride [$\text{AgCl}_{(\text{s})}$]... $\text{NaCl}_{(\text{aq})} + \text{AgNO}_{3(\text{aq})} \rightarrow \text{AgCl}_{(\text{s})} + \text{NaNO}_{3(\text{aq})}$

The equivalence point of this reaction is indicated by the addition of potassium chromate indicator, which forms a deep red/brown compound when it reacts with any excess $\text{AgNO}_{3(\text{aq})}$.

The Titration:

- a 16.8 g sample of biscuit is crushed and dispersed in distilled water.
- the mixture is filtered into a 200 ml volumetric flask, the biscuit residue and glassware washed with successive 10 ml portions of distilled water, the washings collected in the volumetric flask
- the volumetric flask is filled to exactly 200.0 ml with distilled water
- duplicate 25.00 ml aliquots of the diluted sample are pipetted into conical flasks and potassium chromate indicator added
- the aliquots are titrated with 0.102 M $\text{AgNO}_{3(\text{aq})}$ solution and concordant titres of 14.25 ml and 14.30 ml are obtained.

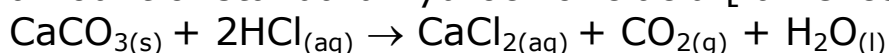
The Calculation:

- balanced equation: $\text{NaCl}_{(\text{aq})} + \text{AgNO}_{3(\text{aq})} \rightarrow \text{AgCl}_{(\text{s})} + \text{NaNO}_{3(\text{aq})}$
mol ratio 1 : 1
- average titre = $[(14.25 + 14.30)/2] = 14.275 \text{ ml} = 0.014275 \text{ L}$
- amt. of 0.102 M $\text{AgNO}_{3(\text{aq})}$ **n = CV** = $0.102(0.014275) = 0.001456 \text{ mole}$
- amt. of NaCl in 25 ml aliquot = 0.001456 mole [1:1 mole ratio]
- amt. of NaCl in 200 ml flask = $0.001456 \times 200.0/25.00 = 0.011648 \text{ mole}$
- amt. of NaCl in 16.8 g of biscuit = 0.011648 mole
- mass NaCl in 16.8 g biscuit **m = nM_r** = $0.011648(58.44) = 0.680709 \text{ g}$
- % [w/w] NaCl in biscuit = $[0.680709/16.8] \times 100 \approx 4.05\%$

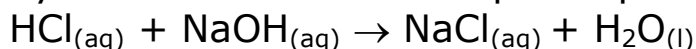
Example of Volumetric Analysis #4 [back titration]

The % Calcium in limestone

The calcium carbonate in a crushed limestone sample is determined by volumetric analysis. The calcium carbonate is first reacted with a measured amount of standard hydrochloric acid [an excess] ...



The excess hydrochloric acid is then titrated with standardised sodium hydroxide solution to the phenolphthalein endpoint ...



The Titration:

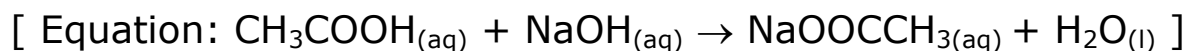
- a 1.050 g sample of limestone is weighed into a 250 ml conical flask
- a 50.00 ml aliquot of 0.500 M $\text{HCl}_{(aq)}$ solution is pipetted into the flask
- 5 drops of phenolphthalein indicator are added when reaction ceases
- a burette is rinsed and filled with standardised 0.500 M $\text{NaOH}_{(aq)}$ solution
- the initial burette reading is recorded as 2.05 ml
- the excess $\text{HCl}_{(aq)}$ is then titrated to the first permanent pink colour
- the final burette reading is recorded as 25.45 ml.

The Calculation:

- titre $\text{NaOH}_{(aq)} = 25.45 - 2.05 = 23.40 \text{ ml} = 0.02340 \text{ L}$
- amt. of NaOH in titre **$n = CV$** $= 0.500(0.02340) = 0.01170 \text{ mole}$
- amt. of excess $\text{HCl}_{(aq)} = 0.01170 \text{ mole}$ [1:1 mole ratio]
- amt. $\text{HCl}_{(aq)}$ added to flask **$n = CV$** $= 0.500(0.0500) = 0.02500 \text{ mole}$
- amt. $\text{HCl}_{(aq)}$ reacting with $\text{CaCO}_{3(s)} = \text{HCl added} - \text{HCl excess}$
 $= 0.02500 - 0.01170 = 0.0133 \text{ mole}$
- balanced equation: $\text{CaCO}_{3(s)} + 2\text{HCl}_{(aq)} \rightarrow \text{CaCl}_{2(aq)} + \text{CO}_{2(g)} + \text{H}_2\text{O}_{(l)}$
mol ratio 1 : 2
- amt. $\text{CaCO}_3 = \frac{1}{2} \text{ mole HCl reacted} = \frac{1}{2}[0.0133] = 0.0066566 \text{ mole}$
- mass CaCO_3 **$m = nM_r$** $= 0.0066566(100.1) = 0.66566$
- % [w/w] CaCO_3 in sample $= [0.66566/1.050] \times 100 \approx 63.4\%$

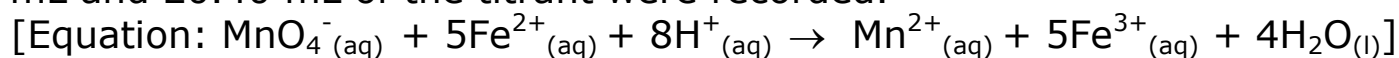
Examples of Volumetric Analysis:

1. A 10.00 mL aliquot of vinegar was pipetted into a conical flask, phenolphthalein added, and the contents titrated with 0.0560 M NaOH. Titres of 16.70 mL and 16.75 mL were obtained.



What is the %[w/v] ethanoic acid in the vinegar?

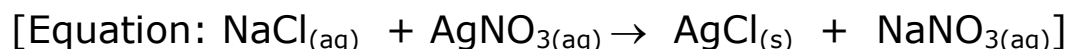
2. Duplicate 20.00 g samples of crushed rock were accurately weighed into conical flasks and dissolved in 10% sulfuric acid solution. The resulting mixtures were titrated with 0.125 M $\text{KMnO}_{4(\text{aq})}$ solution. Titres of 20.30 mL and 20.40 mL of the titrant were recorded.



What is the %[w/w] iron in the rock sample?

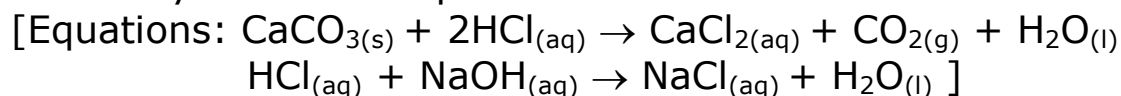
3. A 16.8 g sample of biscuit was weighed out and dispersed in distilled water. The mixture was filtered into a 200 mL volumetric flask. The biscuit residue and glassware were washed with distilled water and the washings collected in the volumetric flask. The volumetric flask was then made up to volume with distilled water.

Duplicate 25.00 mL aliquots of the diluted biscuit mixture were pipetted into conical flasks and potassium chromate indicator added. The aliquots were then titrated with 0.102 M $\text{AgNO}_{3(\text{aq})}$ solution. Concordant titres of 14.25 mL and 14.30 mL were obtained.



What was the %[w/w] NaCl in the biscuit?

4. A 1.05 g sample of limestone was reacted with a 50.00 mL aliquot of 0.500 M hydrochloric acid. After the reaction had ceased, the excess acid was back titrated with 0.500 M $\text{NaOH}_{(\text{aq})}$ solution to the bluish bromothymol blue endpoint. A titre of 23.40 mL was obtained.



What was the % [w/w] CaCO_3 in the limestone?
