Summary sheet of volumetric analysis.

Know your equipment and definitions

Burette – glassware that delivers an *accurate variable* volume of liquid. Usually contains a solution with an accurately known concentration. This solution is known as a standard solution, see below.

Titre - The volume of solution delivered by the burette, as shown on the right, in order to reach the end point.

Concordant titres – titres whose highest value differs from the lowest value by no more than 0.10 mL.
eg 21.80 mL, 21.75 mL, 20.70 mL.
Only concordant titres are used to obtain an average titre.

Pipette – an instrument that delivers an *accurate fixed* volume of solution. For example a 25mL pipette is used to deliver exactly 25.00mL and a 10 mL pipette will deliver exactly 10.00 mL. The pipette is calibrated to leave a small volume of solution in the tip of the pipette. The user should not try to dispense this into the flask.

Aliquot – an ***accurate fixed*** volume of solution delivered using a pipette.

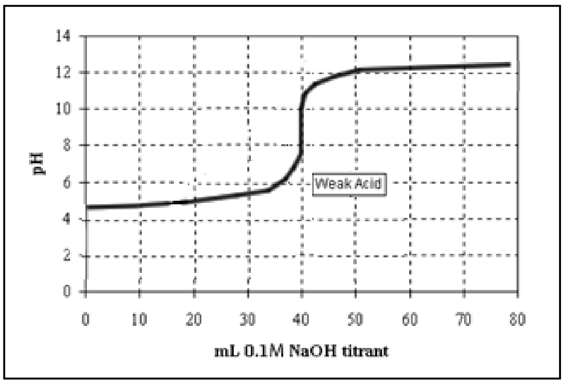
Volumetric flask – Is used to dilute concentrated solutions or prepare standard solutions.

Standard solution – A solution whose concentration is accurately known, This solution usually goes into the burette
Primary standard – A substance that is used to make a standard solution. A primary standard should:

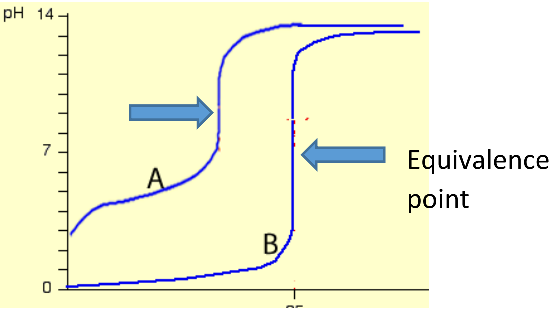
- have a high molecular mass. This will reduce the error in calculations.
- have a known formula mass.
- have a high degree of purity.
- not react with the atmosphere or decompose
- be highly soluble

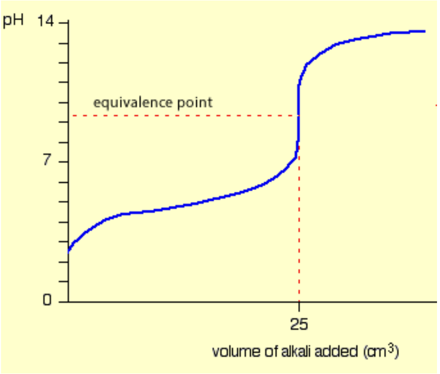
Equivalence point – Is a point in the titration where the mol of the titrant is in the exact stoichiometric ratio as the mol of the substance being titrated. In other words, the reaction is complete as all the substance in the conical flask has fully reacted with the substance titrated from the burette. The equivalence point is not obvious to the person performing the titration.
End point – Is a point in the titration where the indicator changes colour to signal the end of the titration procedure. Ideally the end point should be reached in the next drop delivered by the burette.
Indicator – is a substance that changes colour within a certain pH range and is used to indicate the end point of a titration. Ideally the indicator should change colour as close to the equivalence point as possible.

Ph Curve - shows how the pH of a solution in the conical flask changes as the titration proceeds. The pH curve, shown on the right, is of a titration titrating a weak acid against a strong base. Such pH curves are useful in selecting an appropriate indicator.



What can a pH curve tell us? Consider the pH curve shown on the right of a titration of two monoprotic acids. Information that can be obtained from the curves includes:
- The strength of the acid or base used. Judging by the shape of each curve we can tell that A is a weak acid and B is a strong acid. The final pH of around 13 indicates that the base used is a strong base.
- The equivalence point of a weak acid vs strong base titration is above pH 7 while the equivalence point of strong acid is around pH 7.
- Judging by where the equivalence point is on the curve an appropriate indicator can be found.





The reason why the equivalence point is not always at pH 7 is linked to the conjugate acids and bases of the reactants.
For example, consider the titration of acetic (ethanoic acid) with NaOH, the pH curve is shown on the right.
The reaction between acetic acid and NaOH is given below.
CH_3COOH (aq) + OH^- (aq) → CH_3COO^- (aq) + H_2O(l)
CH_3COO^- is a medium strength base so at the point where CH_3COOH and OH^- have reacted in the stoichiometric ratio, shown by the balanced chemical equation, the solution will have acetate (CH_3COO^-) ions present thus forming a basic or alkaline solution.
Just to summarise:
-- when titrating a strong acid with a strong base, pH = 7 at equivalence point
-- when titrating a weak acid with a strong base, pH > 7 at equivalence point
-- when titrating a strong acid with a weak base, pH < 7 at equivalence point

Examples of a weak acid include.
- HF, CH_3COOH, H_2CO_3, H_3PO_4

Examples of strong acid
- HCl, H_2SO_4 , HNO_3

Examples of weak base
- NH_3

Examples of a strong base
- KOH, NaOH, LiOH

Summary of strength of acid and conjugate base
strong acid has a weak conjugate base eg
HCl + OH^- → Cl^- + H_2O
Weak acid has strong conjugate base eg
H_2CO_3 + $2OH^-$ → $2H_2O$ + CO_3^{-2}

In a titration two things are needed to calculate the concentration of the unknown solution.

1 – The exact volume of the standard solution delivered.
  - With which to calculate the mol of primary standard delivered in each titre.

2 – A balanced chemical equation for the reaction between the reactants in each solution.
  - A balanced chemical equation will give the stoichiometric ratio between the two reactants, hence knowing the mole of primary standard we can find the mole of unknown present.

Errors

Washing glassware

- Burette- always rinsed with the solution that will be delivered by the burette.
  errors – rinsing with water – dilutes the solution in the burette.
  impact on titre – increased
- Pipette – washed with the solution it will deliver
  errors – rinsing with water – dilutes the solution in the pipette
  impact on titre – decrease

- Flask – can be washed with water.
- Volumetric flask – can be washed with water.

Reading the burette.

- Eye level with the meniscus.
- Take reading from the bottom of the meniscus.
- Give the reading to two decimal places
- Error is +/- 0.05mL (half of the smallest graduation)

Calculations in volumetric analysis.

On the next page are some examples and techniques that may help you to unpack a volumetric analysis question that involves titration with and without dilution prior to titrating.

When answering a volumetric analysis question involving many steps of dilution of the original sample a diagram is essential to back track. Consider the example below.

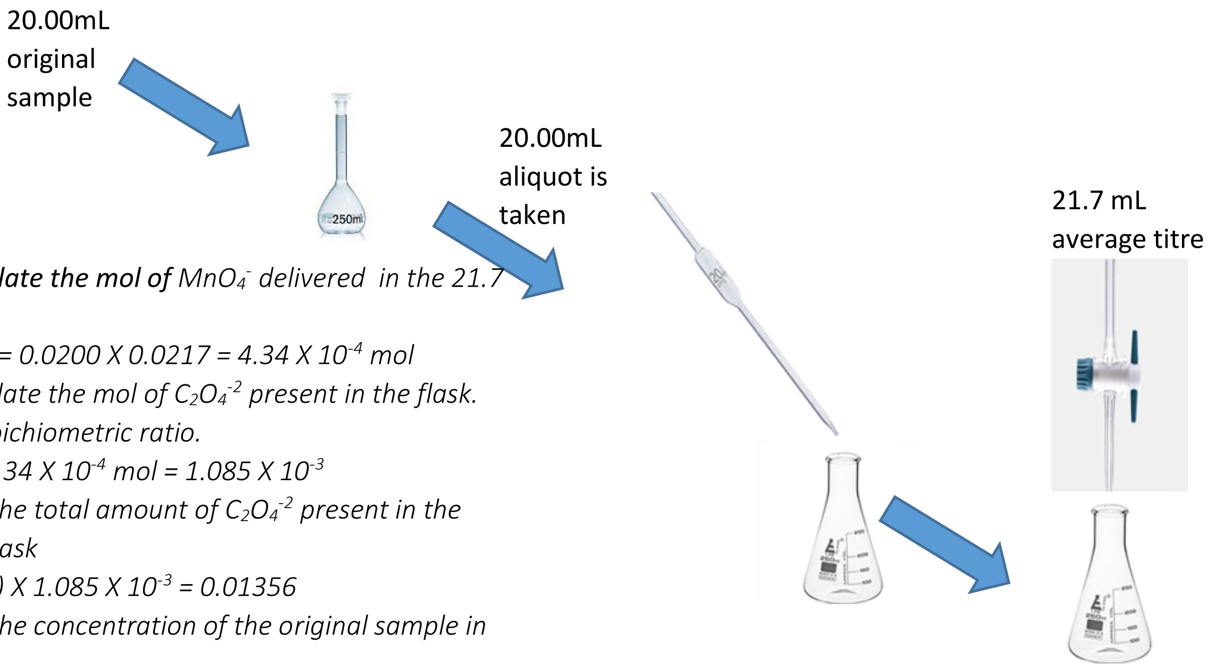
A clear, colourless liquid extract of the rhubarb plant was analysed for the concentration of oxalic acid, $H_2C_2O_4$, by direct titration with a recently standardised and acidified potassium permanganate solution, $KMnO_4(aq)$. The balanced equation for this titration is shown below.

$$\underset{\text{purple}}{2MnO_4^-(aq)} + \underset{\text{colourless}}{5C_2O_4^{2-}(aq)} + 16H^+(aq) \rightarrow \underset{\text{colourless}}{2Mn^{2+}(aq)} + 10CO_2(g) + 8H_2O(l)$$

The steps in the titration were as follows:
Step 1 – A 20.00 mL aliquot of the rhubarb extract was placed in a 250 mL volumetric flask and made to the mark with distilled water
Step 2 – A 20.00 mL aliquot of the diluted rhubarb extract from the volumetric flask was placed in a 200 mL conical flask.
Step 3 – The burette was filled with acidified 0.0200 M $KMnO_4$ solution.
Step 4 – The acidified 0.0200 M $KMnO_4$ solution was titrated into the rhubarb extract in the conical flask. The titration was considered to have reached the end point when the solution in the conical flask showed a permanent change in colour to pink. The volume of the titre was recorded.
Step 5 - The titration was repeated until three concordant results were obtained. The average of the concordant titres was 21.7 mL.

Find the concentration of $H_2C_2O_4$ in the original sample of rhubarb extract in %(w/v)

Unpacking all this information is difficult so draw a flow diagram.



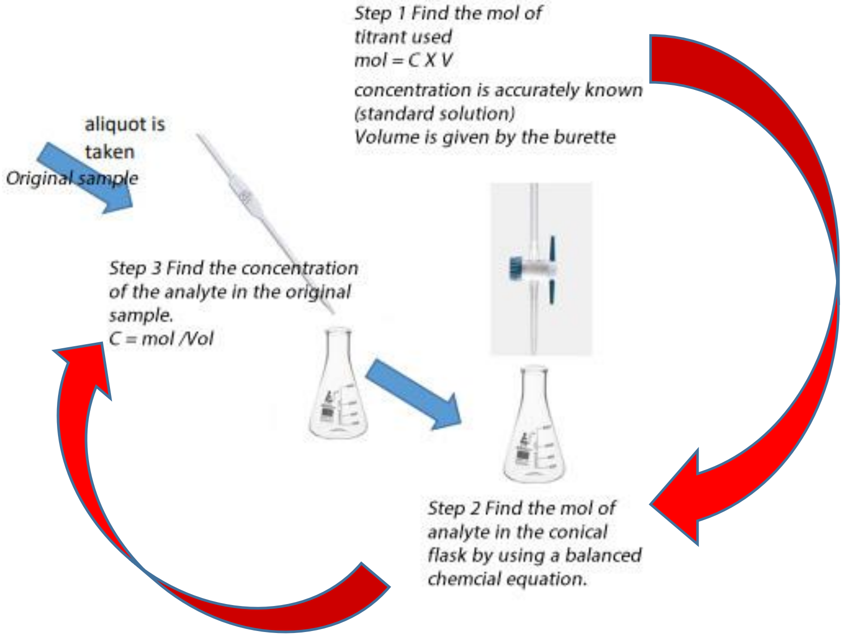
Step 1 Calculate the mol of *MnO_4^- delivered in the 21.7 mL titre.*
=> $n = C \times V = 0.0200 \times 0.0217 = 4.34 \times 10^{-4}$ mol
Step 2 Calculate the mol of $C_2O_4^{-2}$ present in the flask.
using the stoichiometric ratio.
=> $(5/2) \times 4.34 \times 10^{-4}$ mol $= 1.085 \times 10^{-3}$
Step 3 Find the total amount of $C_2O_4^{-2}$ present in the volumetric flask
=> $(250 / 20) \times 1.085 \times 10^{-3} = 0.01356$
Step 4 Find the concentration of the original sample in %w/v
=> mass of *$H_2C_2O_4 = 0.01356 \times 90.0 = 1.22$ grams*
=> $(1.22 / 20.00) \times 100 = 6.10$ %(w/v)

When the question requires no dilution of the original sample before titration only three steps are required, as shown on the right.

step 1 - find the mol of titrant by using the concentration of the standard solution and the average titre.

Step 2 - find the mol of analyte by using the stoichiometric ratio from a balanced chemical equation

Step 3 – find the concentration of the analyte in the original sample by using the mol of analyte in the conical flask and the volume from which it came from.



Step 1 Find the mol of titrant used
mol = C X V
concentration is accurately known (standard solution)
Volume is given by the burette

Step 2 Find the mol of analyte in the conical flask by using a balanced chemcial equation.

Step 3 Find the concentration of the analyte in the original sample.
C = mol /Vol

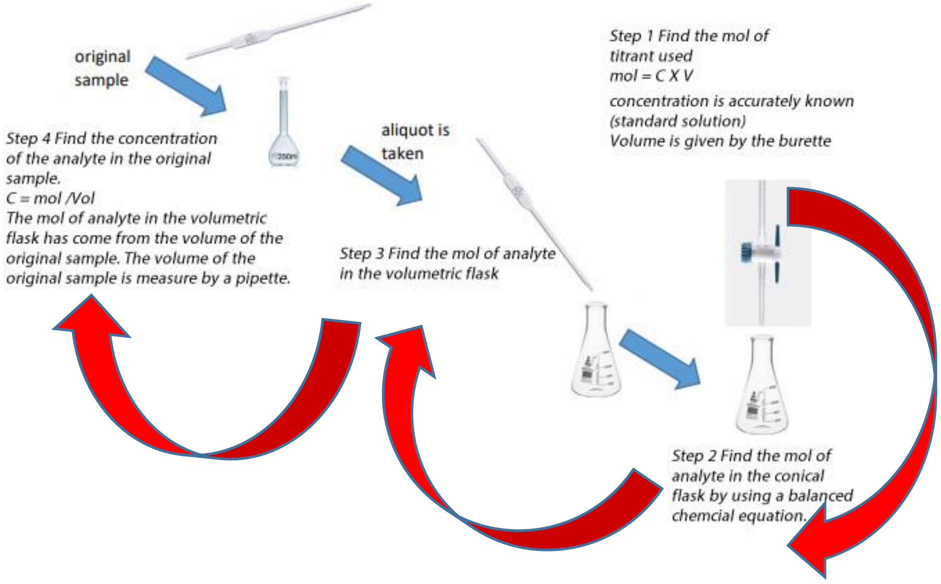
If the question, however, required dilution of the original sample before titration, four steps are required as shown on the right.

step 1 - find the mol of titrant by using the concentration of the standard solution and the average titre.

Step 2 - find the mol of analyte by using the stoichiometric ratio from a balanced chemical equation

Step 3 – find the concentration of the analyte in the volumetric flask multiplying the mol of analyte in the conical flask(step 2) by the ratio (volume of volumetric flask/volume of aliquot delivered into the conical falsk)

Step 4 – find the concentration of analyte in the original sample using the mol of analyte in the volumetric flask (step 3) and the volume of sample diluted using the volumetric flask.



Step 1 Find the mol of titrant used
mol = C X V
concentration is accurately known (standard solution)
Volume is given by the burette

Step 2 Find the mol of analyte in the conical flask by using a balanced chemcial equation.

Step 3 Find the mol of analyte in the volumetric flask

Step 4 Find the concentration of the analyte in the original sample.
C = mol /Vol
The mol of analyte in the volumetric flask has come from the volume of the original sample. The volume of the original sample is measure by a pipette.

Try the two exercise on this worksheet Solution are given.