Titration Principles

General Principles

Volumetric analysis refers to a collection of methods in which the volume of a solution of accurately known concentration, **the standard solution**, required to react quantitatively with the analyte is determined. The process is known as **titration.**

- Standard solution is generally added from the burette (but not always)
- The solution in the burette is termed the **titrant**
- **Equivalence point** is the point at which the analyte is totally consumed
- **Endpoint** is where there is an observable change in the system such as colour change of an indicator. This point should be very close to the equivalence point.
- As a general rule the volume of titrant should be within 15-30 mL. Less than this volume introduces considerable relative errors and more than this volume is time and chemical consuming.

Titration standards

Commonly available standards, (such as sodium hydroxide and hydrochloric acid) are generally not found in an extremely pure form. Solid sodium hydroxide is very hygroscopic and also absorbs carbon dioxide from the air forming sodium carbonate. Hydrochloric acid is provided as a concentrated solution of approximately known concentration. This means that it is not possible to measure out exact quantities.

A **primary standard** enables the chemist to determine exactly the concentration of another solution which is termed **the secondary standard.**

A primary standard should have:

- **High purity** so that the mass of material can be weighed out and the exact number of moles determined ie it must be 100% pure
- **Stability** and not degrade with time by absorption of moisture from the atmosphere or be easily oxidised
- **Absence of hydrate water** which would not allow the exact composition to be known
- **Availability at reasonable cost**
- **Reasonable high formula mass** to reduce weighing errors involved in small masses.

The value of the secondary standard should remain constant for a considerable time before restandardisation is required. Sodium hydroxide, a common secondary standard for the analysis of acidic solutions has been shown to change its concentration by 0.1-0.3% per week during storage in a glass bottle. This is primarily due to absorption of CO_2 but also due to reaction of NaOH with the glass to form sodium silicate (a compound which causes glass stoppers to “freeze” when used with alkaline solutions.

Reactions Used in Volumetric Analysis

There are limited reactions suitable for titration. Criteria used to define suitable titrations include:

1. **Defined stoichiometry:** A balanced equation must be written that describes the reaction correctly as the reaction ratio must be known for the calculations.
2. **Rapid reaction rate** so that a premature endpoint is not obtained by a lag in the reaction.
3. **Complete reaction** so that the analyte is completely consumed
4. **Endpoint detection** must be available to accurately determine the equivalence point

Types of Volumetric Analysis

Table 2.1 Major types of volumetric analysis

Type	Mechanism	Example
Acid – Base	Involves transfer of a proton from the acid to the base	Acids in wine by titration with standard NaOH solution
Oxidation –Reduction (commonly referred to as REDOX reactions)	Involves transfer of electron from one species to another	Iron II can be analysed by oxidation with a known volume of standardised permanganate solution
Precipitation	Involves removal of the analyte as a precipitate	Analysis of salt levels by precipitation of chloride using standard silver nitrate solution
Complex formation	Metal ions form complex by bonding to ligands which have pairs of unbonded electrons	Determination of water hardness by titration with EDTA

Endpoint Determination
Question: When has enough titrant been added to completely consume the analyte?
Answer: At the equivalence point
Question: How is this point determined?
Answer: By some visual indication as indicated below

1. **Addition of a colour-change indicator**
    - Addition to the titration flask of a species which changes colour when either the titrant is in excess or the analyte disappears. (Phenolphthalein is an indicator which changes colour between pH 8.2-10…… which coincides with the equivalence point of a number of acid/base reactions
    - The endpoint colour change and the equivalence point should be very close otherwise an **indicator error** is introduced
    - Colour change should be very obvious.

2. **Self indicating reaction**
    - Ideal situation if the analyte or titrant changes colour and the change can be seen. Potassium permanganate changes from an intense purple colour to colourless when it forms manganese II ions

3. **Electrical measurement of solution**
    - Where a suitable indicator is not available measurement of solution potential, current or resistance changes may be measured during a titration. These methods provide a very accurate endpoint determination but can be costly and time consuming. (These type of measurement will be studied in Instrumental Tests 3)

The endpoint detection is the most inaccurate step in a titration. Even the best technique could not hope to determine the endpoint to a greater accuracy than 0.05 mL and typically it is 0.1 mL. Conversion of this into relative error (for a 25.0 mL titre), 0.4%, indicates it is much greater than errors introduced by weighing or pipetting.

Calculations
Titration calculations revolve around the number of moles of the reactants. (See chapter 4 of Calibration and Data Handling notes).

Remember these formula

MOLES = MASS (g) ÷F Wt

And

MOLES = Molarity x Volume (L)

The method for calculations in volumetric analysis revolves around these equations and a balanced reaction equation.

Steps in a titration calculation

Step 1 Write a balanced equation for the reaction

Step 2 Calculate the number of moles of the standard reactant

Step 3 Determine the number of moles of the analyte, by using the reaction ratio

Step 4 Calculate the mass of the analyte (or the unit required)

Example:
A solution of approximately 0.1 M HCl is standardised with Na_2CO_3. 0.1472 g of Na_sCO_3 requires 23.7 mL of the HCl to reach endpoint. The HCl is then used to titrate a solution of NaOH. 25.0 mL of the base solution is titrated to endpoint by 15.9 mL of the acid. What is the concentration of the NaOH?

Part I
Step 1: write the balanced equation for the reaction

Step 2: calculate the number of moles of the standard reactant (you must firstly decide which species is the standard and which is the analyte)

Step 3: determine the number of moles of the analyte by using the reaction ratio

Step 4: Calculate the concentration

Part 2
Step 1: write the balanced equation for the reaction

Step 2: calculate the number of moles of the standard reactant (you must firstly decide which species is the standard and which is the analyte)

Step 3: determine the number of moles of the analyte by using the reaction ratio

Step 4: Calculate the concentration

Back Titrations
Reactions which are slow or produce side-reactions can prove difficult for titration. For example:

- **Calcium carbonate** is a water insoluble base. It will react with HCl but provides a false endpoint as the HCl reacts with the solid
- **Ammonia** is a gas not completely soluble in water with some of the gas lost as a gas.
- **Vitamin C** (ascorbic acid) is stable in the solid state but is readily oxidised in solution by the oxygen in the air. Any attempt to titrate a solution of it with an oxidising titrant such as iodine or permanganate will be inaccurate because the analyte is not only reacting with the titrant.

The procedure known as **back titration** enables analyses such as those listed above to be conducted with a high level of accuracy. A known amount of some reagent which reacts with the analyte is added and a titration of the left over reagent is done. The analyte **is not** titrated. The method overcomes slow reactions and side reactions.

The calculations are a little more complicated, but not more difficult if an understanding of the process occurs. Use the following example to gain an understanding of the process. You will gain practise in the method during the practical sessions.

In the analysis of limestone for calcium carbonate:

- Dissolution will not occur in water but it will occur in HCl
- HCl becomes the solvent
- Excess HCl is quantitatively added to the limestone
- HCl reacts with the calcium carbonate (it may require gentle heating to speed up the reaction and drive off the carbon dioxide)
- Some HCl remains
- Amount of HCl remaining is determined by titration with standard NaOH
- Number of moles of $CaCO_3$ in the original sample are calculated.

Steps in a back titration calculation
Step 1 Write a balanced equation for both reactions

Step 2 Calculate the number of moles of the standard "solvent" added to the sample

Step 3 Calculate the moles of titrant used in the back titration

Step 4 Calculate the moles of "solvent" that reacted in the back titration

Step 5 Calculate the moles of "solvent" that reacted with the analyte (Step 2-Step4)

Step 6 Calculate the moles of analyte that reacted with the "solvent"

Step 7 Calculate the mass of analyte

Example:
The content of calcium carbonate, an insoluble basic analyte in limestone, is analysed by back titration. 0.2160 g of the sample is powdered and dissolved in 50.0 mL of0.103M HCl solution. The reaction mixture is heated and stirred to ensure a rapid and complete reaction between the $CaCO_3$ and the HCl. After cooling, the remaining HCl is back titrated with 21.0 mL of 0.0978 M NaOH.

Step 1 *Write a balanced equation for both reactions*

Step 2 *Calculate the number of moles of the standard "solvent" added to the sample*

Step 3 *Calculate the moles of titrant used in the back titration*

Step 4 *Calculate the moles of "solvent" that reacted in the back titration*

Step 5 *Calculate the moles of "solvent" that reacted with the analyte (Step 2-Step4)*

Step 6 *Calculate the moles of analyte that reacted with the "solvent"*

Step 7 *Calculate the mass of analyte*

Advantages and Disadvantages of Titrimetric Analysis

Time:

- Requires a standardisation step to obtain the exactly known concentration of the standard solution
- Individual titration is generally rapid and should be completed within 10 minutes, excluding sample preparation.

Sensitivity:

- Requires fairly concentrated samples to be successful. Generally limited to a lower level of 0.001M and an upper level of 0.5M

Accuracy:

- Is dependent on the accuracy of the standard solution
- Also dependent on the availability of an endpoint determination close to the equivalence point
- Can obtain accuracies of better than 1%

Specificity:

- NaOH will react with all acidic species….. it is unable to differentiate between a combination of acidic species within the one sample
- Removal of most interferents is well documented
- Specificity can be increased by altering the method ……EDTA can be made specific for calcium and magnesium by adjusting the pH

Cost:

- Relatively cost effective in terms of equipment for general titration with indicator endpoints
- Costs are increased if an electrical means of endpoint detection is required.

QUESTIONS

Concepts

1. What is the difference between endpoint and equivalence point?
2. Explain why titration volumes should be between 15 and 30 mL
3. Why is a solution of sodium hydroxide unsuitable as a primary standard
4. The reaction between ethanol and an organic acid (eg ethanoic acid) takes about 6 hours at boiling point. The reaction achieves a conversion of approximately 70%. Comment of the suitability of this reaction as a titration reaction.
5. For the following descriptions, identify (i) the primary standard, (ii) the standard solution and (iii) the analyte
   (a) the calcium ion content of a solution is determined by titration with EDTA, which has been standardised with a solution prepared from accurately weight zinc pellets
   (b) A silver nitrate solution is added to a weighed mass of pure sodium chloride until endpoint is reached. The silver nitrate solution is then used to analyse the chloride ion concentration of a sample.

Applications

6. Calculate the molarity and g/L of analyte in the following titrations.

	Volume of sample (mL)	Volume of titrant (mL)	Molarity of titrant	1 mole of analyte reacts with how many moles of titrant	Formula weight of analyte
A	10	15.6	0.104	1	60
B	25	31.3	0.0589	2	134
C	20	22.5	0.211	0.5	100
D	25	26.9	0.107	0.4	207

7. Calculate the %w/w of analyte in the following back titrations. Note that all back titration ratios are 1:1 and 50 mL of standard :solvent" are used in each case.

	Mass of sample	Molarity of "solvent"	Volume of titrant (mL)	Molarity of titrant	1 mole of analyte reacts with how many moles of "solvent"	Fw of analyte
A	0.4521	0.116	23.4	0.0997	1	100
B	1.1282	0.103	19.8	0.104	1.5	84
C	1.3294	0.212	31.2	0.108	2	120
D	0.3915	0.0123	17.7	0.0109	0.5	66
E	0.2688	0.0245	20.1	0.0321	0.6	80