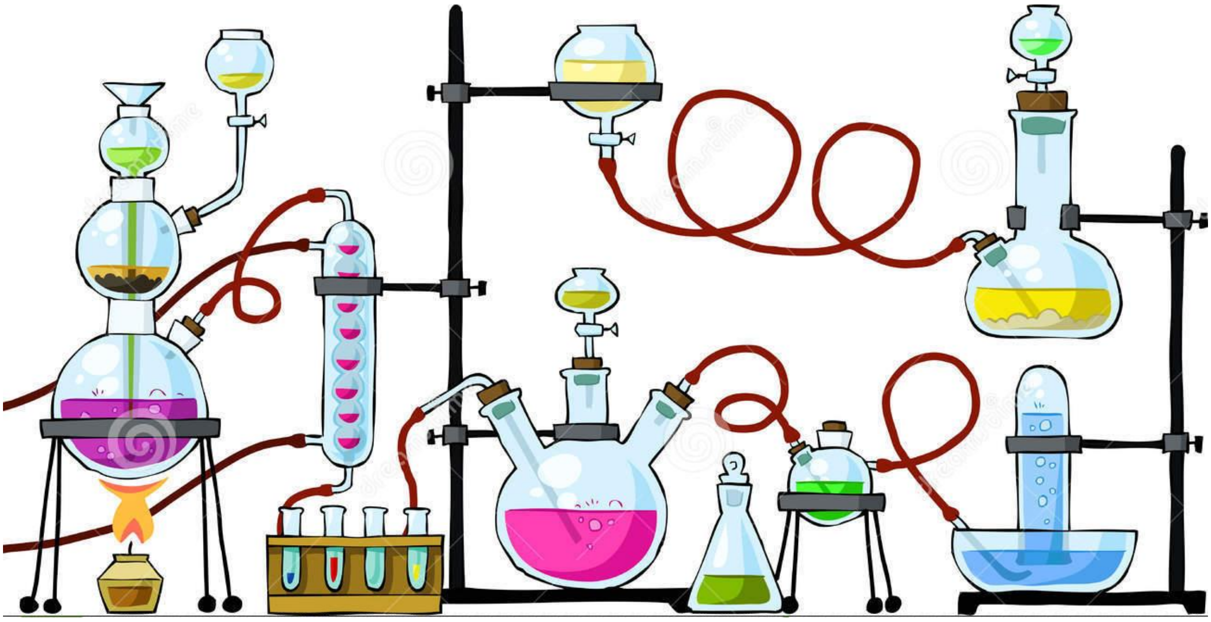
CfE Advanced Higher Chemistry

Grove Academy



Researching Chemistry

Learner Workbook

Electronic version

Version 3 (May 2017)

Researching Chemistry

1. Introduction

The purpose of this unit is to allow you to become familiar with a variety of practical techniques used in conducting chemical research and to gain experience and practice in the measurements and associated calculations done in support of practical chemistry. You will use the skills acquired in this unit in the completion of a project later in the year.

This unit is divided into sections relating to ***4 key areas***

- **Gravimetric analysis**
- **Volumetric analysis**
- **Practical skills and techniques**
- **Stoichiometric calculations**

By completion of the advanced higher chemistry course you should have had the opportunity to carry out the following techniques. Keep note, using your own checklist in your lab book as you complete each one

Checklist

(a) Use of a Balance
(b) Standardisation
(c) Control/ Reference
(d) Complexometric titration
(e) Back titration
(f) Colorimetry/ serial dilution
(g) Distillation
(h) Refluxing
(i) Vacuum filtration
(j) Recrystallisation
(k) % yield
(l) TLC
(m) Melting point determination
(n) Separating funnel

1a. The stoichiometric equation

This section of the course relies on the ability to write formulae and balanced equations correctly.

Any reaction in which the substances react completely according to the mole ratios given by a balanced (stoichiometric) equation is called a **quantitative reaction**.

When a quantitative reaction takes place, an analysis of the reaction can be undertaken and one unknown value can be determined. Two chemical methods of analysis are **volumetric** (involving accurately measured volumes of solutions) and **gravimetric** (involving accurate weighing of materials).

1a. The stoichiometric equation

Write a brief note in your theory jotter

- Explain what is meant by a **stoichiometric equation**.
- What information is contained in a **stoichiometric equation**?
- Explain what is meant by a **quantitative reaction**.

Exercise A – Balancing equations revision

Balance the following equations

1. $CHCl_3 + NaOH \longrightarrow HCOONa + NaCl + H_2O$
2. $Al + NH_4ClO_4 \longrightarrow Al_2O_3 + AlCl_3 + NO + H_2O$
3. $BF_3 + NaBH_4 \longrightarrow B_2H_6 + NaBF_4$
4. Ozone reacts with potassium iodide and water to form iodine, oxygen and potassium hydroxide

1b. Gravimetric analysis

Gravimetric analysis is a method for the analysis of **the mass of an element or compound present in a substance.** It usually involves changing a substance of unknown composition into another substance of **known chemical composition** that can be readily isolated, purified and weighed. The accuracy of this method depends on the accuracy of the balance used and the dexterity of the person carrying out the procedure. Weighing of samples in the lab can be done in one of two ways.

(i) weighing by tare

A clean dry container is placed on the balance and then the balance is zeroed (tared). Then, using a spatula, a sample is added to the container.

The accurate mass of the contents is then measured and recorded.

(ii) weighing by difference

A clean dry weighing bottle is first weighed empty and then, using a spatula, a sample is added to it.

The accurate mass of the weighing bottle and its contents is then measured and recorded.

The next step is to transfer the sample from the weighing bottle to the container to be used in the experiment.

Gentle tapping on the base of the weighing bottle will ensure that the bulk of the sample is transferred but it is unimportant if traces of the sample remain.

Finally, the weighing bottle and any residual material are accurately weighed and the mass recorded.

The accurate mass of the sample transferred is the **difference** between the two recorded masses.

1b. Gravimetric analysis

Write a brief note in your theory jotter

- Explain how to weigh a sample

  (i) **by difference**

  (ii) **by tare**

Gravimetric analysis frequently involves **precipitation** (production of an insoluble product from soluble reactants) followed by **filtration**. The product must:

- have a **low solubility** so that the entire product is precipitated

- have a particle size that is not too small to allow **easy filtration**
- be **stable** at temperatures of 100–105°C (to be dried in an oven)

The accuracy of this method relies on the use of reactants at high purity, reactions going to completion (not being equilibria) and having no side reactions. Additionally, the procedure must be carried out extremely carefully so that all of the material is transferred from the reaction vessel to the filtration apparatus (called mass transfer losses). The apparatus must then be dried and weighed with no further loss of residue during transfer.

1b. Gravimetric analysis

Write a brief note in your theory jotter

- Use an example to explain what is meant by a **precipitation reaction**.
- Explain what is meant by **gravimetric analysis**.
- What **properties** of a product makes it suitable for gravimetric analysis?
- List the main reasons why the **measured** and **calculated** values for the quantity found in an analytical method may be different.

Exercise B – Precipitation problems

1. Write a balanced formula equation, including state symbols, for a compound that could be added to a solution of lead(II) nitrate in order to precipitate the lead from solution? (Refer to page 21 of the data book).

2. Write a balanced formula equation, including state symbols, for the reaction of compound that could be added to a solution of aluminium nitrate and barium nitrate in order to precipitate **only** the barium from solution? (Refer to page 21 of the data book).

3. 10.0 cm^3 of 0·250 $moll^{-1}$ $Na_2CO_3(aq)$ is reacted with excess $CuCl_2(aq)$.

   What mass of precipitate forms?

4. 75.0 cm^3 of 0·750 $moll^{-1}$ $(NH_4)_3PO_4(aq)$ is reacted with excess $FeCl_2(aq)$.

   What mass of precipitate forms?

5. 35.0 cm^3 of a solution of silver(I) nitrate as mixed with an excess of sodium iodide. On filtering and drying to constant mass, 1.233 g of the precipitate was obtained.

   What is the concentration of the silver(I) nitrate solution?

1c. Using gravimetric analysis

Gravimetric analysis requires accurate determination of masses of reactants and products.

A common form of gravimetric analysis involves heating to **change** one substance into another, e.g. dehydration of a hydrated salt to calculate the number of moles of water of crystallization (x).

$$BaCl_2.xH_2O\ (s) \longrightarrow BaCl_2\ (s) + xH_2O\ (g)$$

The completion of this reaction is checked by repeated heating and cooling (the cooling should be in a desiccator) followed by weighing until a **constant mass** is obtained. Successive weighings, at room temperature, should be within 0.01 g of each other.

Example problem 1

Hydrated barium chloride 5.45g was heated strongly in a crucible over a Bunsen flame and heating was continued to a constant mass with cooling in a desiccator. The residue of barium chloride was found to weigh 4.63g.

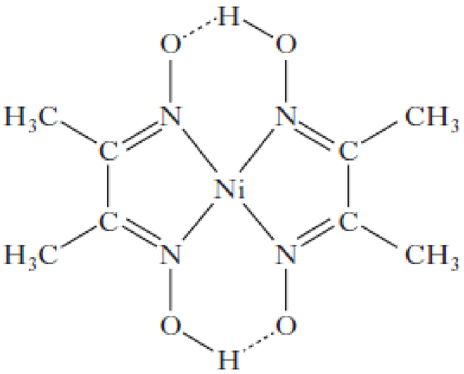
Use the experimental results to establish the formula of the original barium salt.

Example problem 2

1. Nickel(II) ions react quantitatively with dimethylglyoxime ($C_4H_8O_2N_2$) forming a complex which precipitates out as a red solid.

   The equation for the reaction and the structure of the complex are shown below.

$$Ni^{2+} + 2C_4H_8O_2N_2 \longrightarrow Ni(C_4H_7O_2N_2)_2 + 2H^+$$



Relative formula mass = 288·7

When 8.782 g of an impure sample of nickel(II) sulphate, $NiSO_4.7H_2O$, was dissolved in water and reacted with dimethylglyoxime, 8·488 g of the red precipitate was formed.

Calculate the percentage, by mass, of nickel in the impure sample of nickel(II) sulphate.

1c. Using gravimetric analysis

Write a brief note in your theory jotter

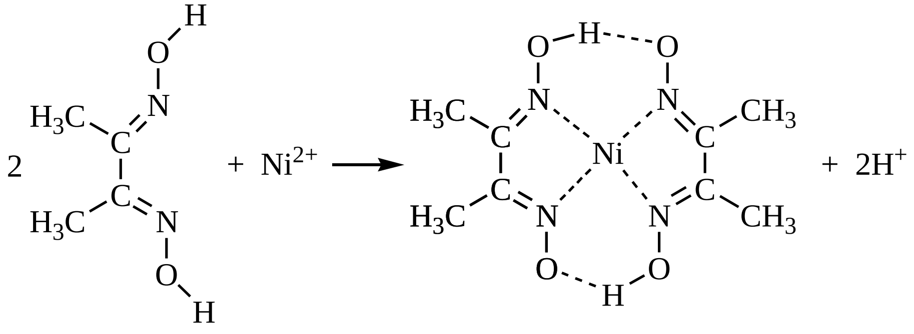
- What **kind** of processes are commonly used in gravimetric analysis?
- Explain what is meant by **heating to constant mass**.
- What is the **acceptable range** for successive weighings to be accepted as constant?

Experiment 1: Analysis of nickel by gravimetric analysis

Aim: To determine the nickel content of nickel chloride by reaction with dimethylglyoxime

Introduction

Gravimetric analysis can be used to determine the nickel content of a nickel(II) salt. This can be achieved by reacting the nickel(II) ions with dimethylglyoxime (butanedione dioxime) in the presence of a slight excess of ammonia:



The complex, nickel(II) dimethylglyoximate, is filtered from the reaction mixture, dried and weighed.

Theoretical % nickel content

- Calculate the formula mass of $NiCl_2.6H_2O$
- Calculate the nickel content as a percentage

Requirements

hydrated nickel(II) chloride ($NiCl_2.6H_2O$)	2 moll^{-1} ammonia
0.1 moll^{-1} dimethylglyoxime in ethanol	2 moll^{-1} hydrochloric acid

500 cm^3 beaker	water pump	weighing bottle	10 cm^3 measuring cylinders
sintered glass crucible	desiccator	hot plate	thermometer
Buchner flask and adapter	balance (+/- 0.001 g)	steam bath	stirring rod
dropper	oven	100 cm^3 measuring cylinders	

Safety

Wear eye protection. If any chemical splashes on the skin, wash it off immediately.

Hydrated nickel(II) chloride is harmful by inhalation and by ingestion. Wear gloves.

Dimethylglyoxime in ethanol is irritating to the eyes and is highly flammable.

2 mol l^{-1} ammonia irritates the eyes.

Procedure

1. Transfer approximately 0.5 g of hydrated nickel(II) chloride to a weighing bottle and weigh the bottle and contents.

2. Add about 20 cm^3 of deionised water to a 500 cm^3 beaker and transfer the bulk of the nickel salt to the water.

3. Reweigh the bottle with any remaining salt.

4. Stir the mixture until the solid dissolves and add about 20 cm^3 of 2 moll^{-1} hydrochloric acid. Dilute the mixture with deionised water to about 200 cm^3.

5. Heat the solution to 70–80°C on a hot plate and add approximately 50 cm^3 of 0.1 mol l^{-1} dimethylglyoxime in ethanol.

6. Add 2 mol l^{-1} ammonia solution dropwise and with constant stirring until a permanent red precipitate is obtained. Add a further 5 cm^3 of the ammonia solution to provide a slight excess. In all, you should have added about 30 cm^3 of ammonia solution.

7. Heat the beaker and contents on a steam bath for about 30 minutes and when the precipitate has settled test the clear liquid for complete precipitation by adding a few drops of the dimethylglyoxime and ammonia solutions.

   If more red precipitate appears then add about 5 cm^3 of 0.1 $moll^{-1}$ dimethylglyoxime solution followed by about 3 cm^3 of 2 $moll^{-1}$ ammonia.

8. Remove the beaker from the steam bath and allow it to cool to room temperature.

9. Dry the sintered glass crucible in an oven at 120°C, allow it to cool in a desiccator & weigh it.

10. Set up the filtration apparatus: sintered glass crucible, Buchner flask and adapter. Filter off the precipitate at the water pump and wash the precipitate with a several portions of deionised water.

11. Dry the crucible and precipitate in the oven at 120°C for about 1 hour and then transfer them to a desiccator.

12. Once they have cooled to room temperature, reweigh the crucible and contents.

13. Heat the crucible and contents to constant mass, i.e. reheat for about 15 minutes in the oven at 120°C, cool in the desiccator and reweigh until two successive readings are within 0.002 g of each other or within 0.01 g of each other if the balance is only accurate to 0.01 g.

14. **Calculate the percentage by mass of nickel** in the sample of the hydrated nickel(II) chloride.

15. Compare this experimental value with the calculated theoretical percentage by mass of nickel. **Account for any difference**.

Analysis of nickel by gravimetric analysis

Using your lab book

- Write a **report** that includes the **aim** of the experiment and the **procedure** written in **impersonal voice**, **past tense** and in enough detail for another member of the class to be able to repeat your work.

- Use a suitable **table** (titled risk assessment) make a note of the **chemicals** used, the main **risks** and the **precautions** to be taken for their use.

1c. Significant figures in chemical calculations

In reporting a measurement, it is important to use the correct number of significant figures – **neither too many nor too few**.

Significant figures are the meaningful digits in a number, i.e. the digits of which we are certain plus the first uncertain digit in the number. E.g. a sample of a chemical was weighed out on a digital balance that read to +/- 0.01 g and the measured mass was 5.37 g. The '5' and the '3' are the certain digits and they are followed by the '7', which is the uncertain digit. So all three digits in the number '5.37' are significant and we say that the number has been quoted to three significant figures.

We can apply a few simple rules in order to achieve this and in what follows the significant figures are shown in bold type:

- Digits that are not zero are always significant. So, 232 cm has 3 significant figures and 3.248 g has 4 significant figures.

- Zeros that lie between non-zero digits are always significant. Thus, 6007 kg has 4 significant figures while 5.08 cm^3 has 3 significant figures.

- Zeros at the beginning of a number are never significant – all they do is set the position of the decimal point. Hence, 0.321 g has 3 significant figures and 0.005 litres has 1 significant figure.

- Zeros at the end of a number are always significant if the number contains a decimal point. Thus, 210.0 mm has 4 significant figures and 0.0600 moll^{-1} has 3 significant figures.

- Zeros at the end of a number may or may not be significant if the number contains no decimal point.

Take the measurement 300 mm, for example – does it have 1, 2 or 3 significant figures?

To decide which is correct you need to know how the measurement was made.

If a ruler capable of measuring to the nearest 10 mm had been used, then the zero immediately following the '3' would be significant but the other zero would not and so 300 mm has 2 significant figures.

This is still ambiguous and to remove that ambiguity it is best to quote the measurement in scientific notation, i.e. as 3.0 x 10^2 mm. It is now clear that this number has 2 significant figures (the exponential part of the number has no bearing on the number of significant figures).

Had the measurement been reported as 3.00 x 10^3 mm, then this number has 3 significant figures and implies that a rule measuring to the nearest mm must have been used.

If no information is given or even suggested about the accuracy of the instrument used to make a measurement, then it is assumed that the trailing zeros in a number with no decimal point are *not* significant.

For example, in the absence of further information, the measurement 2600 kg only has two significant figures – the '2' and the '6'. The zeros that follow are not significant. All shadow of doubt is removed if the measurement is reported in scientific notation, i.e. as 2.6 x 10^3 kg.

Exact numbers

Take the number '10', for example. '10' is an exact number when we use it to describe the number of years in a decade or the number of millimetres in a centimetre. Since there is no uncertainty associated with it, we could in fact write it as 10.00000… with the zeros continuing forever.

Exercise C - significant figures

1. State the number of significant figures in each of the following measurements:

(a) 21 cm

(b) 13.00 g

(c) 0.0055 m

(d) 20.20 cm^3

(e) –0.0037°C

(f) 105.50 kg

(g) 1.03 x 10^{-3} $moll^{-1}$

(h) 5 x 10^3 J

2. Consider the measurement 4000 mg.

a) How many significant figures could 4000 mg have?

b) In the absence of further information, report this measurement in scientific notation showing the correct number of significant figures.

c) If this measurement had been made using a balance that read to +/- 0.1 g, quote the measurement showing the correct number of significant figures.

d) If the measurement had been quoted as 4.00×10^3 mg, state the readability of the balance that must have been used in making the measurement.

Significant figures in calculations

It is important that a calculated result is reported with the correct number of significant figures and this will depend not only on the number of significant figures in the individual measurements but also on the type of mathematical operation being carried out on the measurements.

Multiplication and division

In multiplying and dividing measurements, the *result* must have the **same number of significant figures** as the *measurement* with the **fewest significant figures**.

Example

Calculate the number of moles of solute in 0.0253 litres of a solution with concentration 1.2 moll^{-1}.

number of moles of solute = concentration **x** volume

= 1.2 **x** 0.0253

= 0.0303600 mol (calculator answer)

The concentration measurement has the fewer number of significant figures, i.e. 2, and so, the result must be quoted to 2 significant figures. The answer is therefore rounded off to give:

number of moles of solute = 0.030 mol

Addition and subtraction

The rule to determine the number of significant figures for addition and subtraction is different to that for multiplication and division. In adding and subtracting measurements, the *result* must be reported with the **same number of decimal places** as the *measurement* with the **least number of decimal places**. If a measurement has no decimal place then it will be the limiting factor.

Example

A solution of potassium iodide was prepared by dissolving 2.56 g of the solid in 25.2 g of water.

Calculate the total mass of the solution.

total mass = 2.56 + 25.2

27.76 g

The measurement with the least number of decimal places is the 25.2 g of water and so, according to the above rule, the result must be quoted to 1 decimal place.

Thus, total mass = 27.8 g

Exercise D – applying significant figures

Report each result with the correct number of significant figures.

1. The concentration of magnesium in seawater is 0.00133 mg l^{-1}.

   What mass of magnesium would be present in 6.0 litres of seawater?

2. Given that one mole of potassium chloride has a mass of

   74.6 g, calculate the number of moles of potassium chloride in a 2.0 g sample.

3. What volume of 0.150 $moll^{-1}$ sodium hydroxide solution will contain 0.300 mol of solute?

4. Calculate the mass of one mole of potassium bromide given that the relative atomic masses of potassium and bromine are 39.1 and 79.9 respectively.

5. A weighing bottle containing a liquid sample had a total mass of 15.653 g. After transferring the liquid into a reaction flask, the weighing bottle was reweighed and had a mass of 12.793 g.

   Calculate the mass of liquid transferred to the flask.

Significant figures in more complex calculations

Calculations that involve

- one step but include two or more mathematical operations
- two or more steps.

The rules about significant figures are also applicable when a calculation involves two or more steps.

Postpone rounding off to the correct number of significant figures until the final step.

At least one extra digit beyond the last significant digit should be retained in intermediate results.

This procedure ensures that small errors from rounding off at each step do not combine to affect the final result.

Example 1

In an organic preparation, 8.62 g of benzoic acid were obtained by the hydrolysis of ethyl benzoate.

Calculate the percentage yield of benzoic acid if the theoretical yield was 12.32 g.

$$\%\text{ yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100$$

$$= \frac{8.62}{12.32} \times 100$$

$$= 69.9675\ \%\quad \text{(calculator answer)}$$

In this calculation, the limiting piece of data is the actual yield of benzoic acid, i.e. 8.62 g. It has 3 significant figures and so the final result must be rounded off to 3 significant figures.

% yield = 70.0%

Notice that the number ‘100’ is an exact number and has an infinite number of significant figures.

Example 2

0.53 g of sodium chloride was dissolved in approximately 20 cm^3 of water in a beaker. The solution plus rinsings from the beaker were transferred to a 100 cm^3

volumetric flask. The solution was made up to the graduation mark with water. The flask was stoppered and inverted several times to ensure complete mixing.

Calculate the concentration of the resulting sodium chloride solution.

NaCl: mass of one mole = 23.0 + 35.5 = 58.5 g

no. of moles = $\frac{0.53}{58.5}$

= 0.00906 mol

Although this result should be quoted to 2 significant figures

(0.0091 mol), it is an intermediate one and this is why we carry the extra digit.

concentration = $\frac{n}{V}$

= $\frac{0.00906}{0.100}$

= 0.0906 moll^{-1}

The volume has been quoted to 3 significant figures (0.100 litre) rather than 1 significant figure (0.1 litre). This is because we are told that a 100 cm^3 volumetric flask has been used in the preparation and its accuracy is such that the trailing zeros are significant.

The limiting measurement in this calculation is the mass of sodium chloride (0.53 g) since it has only 2 significant figures. This implies that we cannot justify more than 2 significant figures in the final answer.

concentration = 0.091 moll^{-1}

SQA Marking Instructions relating to significant figures.

Data in question is given to three significant figures.

Correct final answer is 8·16 J.

Acceptable answers - 8·2 J or 8·158 J or 8·1576 J — No penalty.

Final answer 8 J or 8·15761 J — No mark.

i.e. give 1 too few or 2 too many

Exercise E - Significant figures in more complex calculations

Report each result with the correct number of significant figures.

1. The concentration of a hydrogen peroxide solution was determined by titrating 10.0 cm^3 samples of it against 0.106 $moll^{-1}$ acidified potassium permanganate solution. (5 mol of hydrogen peroxide reacts with 2 mol of acidified potassium permanganate).

   The results of two concordant titres are shown below:

	1	2
Initial burette reading/cm^3	5.7	14.0
Final burette reading/cm^3	14.0	22.4

   Use the above data to calculate the concentration of the hydrogen peroxide solution.

2. The masses of copper, zinc and manganese in a sample of an alloy were measured as 1.11 g, 1.1 g and 1 g respectively.

   What is the total mass of the three metals?
3. Calculate the volume of 0.12 $moll^{-1}$ hydrochloric acid required to neutralise 25.0 cm^3 of 0.23 $moll^{-1}$ sodium hydroxide.

Exercise F - Gravimetric analysis calculations

1. A certain barium halide exists as the hydrated salt $BaX_2.2H_2O$, where X is the halogen. The barium content of the salt can be determined by gravimetric methods. A sample of the halide (0.2650 g) was dissolved in water (200 cm^3) and excess sulfuric acid added. The mixture was then heated and held at boiling for 45 minutes. The precipitate (barium sulfate) was filtered off, washed and dried. Mass of precipitate obtained = 0.2533 g.

   i. What is the balanced equation for the reaction?
   ii. How many moles of barium sulfate was produced?
   iii. How many moles of BaX_2 was present at the start?
   iv. What is the gfm of BaX_2?
   v. Determine the identity of X.

2. When a sample of impure potassium chloride (0.4500g) was dissolved in water and treated with an excess of silver(I) nitrate, 0.8402 g of silver chloride was precipitated.

   i. What is the balanced equation for the reaction?
   ii. How many moles of silver chloride was produced?
   iii. How many moles of potassium chloride was present at the start?
   iv. What mas of potassium chloride is this?
   v. What is the percentage potassium chloride in the original sample?

3. Aluminium can be determined gravimetrically by reaction with a solution of 8-hydroxyquinoline (C_9H_7NO). The net ionic equation is:

$$Al^{3+} + 3\ C_9H_7NO \rightarrow Al(C_9H_6NO)_3 + 3\ H^+$$

   A mass of 0.1248 g of $Al(C_9H_6NO)_3$ was obtained by complete precipitation all of the Al^{3+} from a solution prepared by dissolving 1.8571 g of a mineral.

   Show by calculation that the percent mass of aluminium in the mineral sample is 0.395%.

2. Volumetric analysis

Volumetric analysis uses accurately made measurements of volumes and a solution of accurately known concentration in a quantitative reaction to determine the concentration of the other solution used in the reaction.

It is therefore essential that you can calculate the concentration of a prepared solution and be able to dilute a solution to a required concentration.

2. Volumetric analysis

Write a brief note in your theory jotter

- What does **volumetric analysis** involve?

Exercise G – preparing solutions from solids

In all of the following questions, give your answers to 3 decimal places.

1. What mass of sodium carbonate is required to make a 500 cm^3 solution of 0.5 $moll^{-1}$?

2. What mass of ammonium sulfate is required to make a 250 cm^3 solution of 0.1 $moll^{-1}$?

3. What mass of silver(I) nitrate is required to make a 100 cm^3 solution of 0.05 $moll^{-1}$?

4. What mass of potassium permanganate is required to make a 1 litre solution of 0.02 $moll^{-1}$?

Exercise H – preparing solutions by dilution

1. What volume of 0·5 $moll^{-1}$ sodium sulfate is required to make, by dilution with water, one litre of a solution with a **sodium sulfate** concentration of 0·1 $moll^{-1}$?

2. What volume of 0·2 $moll^{-1}$ sodium sulfate is required to make, by dilution with water, one litre of a solution with a **sulfate** ion concentration of 0·08 $moll^{-1}$?

3. What volume of 0·75 moll $^{-1}$ lithium carbonate is required to make, by dilution with water, 300 cm^3 of a solution with a **lithium** ion concentration of 0·25 moll $^{-1}$?

4. What volume of **water** needs to be added to 200 cm^3 of 1.0 $moll^{-1}$ magnesium sulfate solution to produce a solution with a concentration of 0·2 $mol1^{-1}$?

5. What volume of **water** needs to be added to 250 cm^3 of 0·5 $moll^{-1}$ potassium sulfate solution to produce a solution with a **potassium** ion concentration of 0·2 $mol1^{-1}$?

6. What volume of **water** needs to be added to 500 cm^3 of 0·1 $moll^{-1}$ magnesium chloride solution to produce a solution with a **chloride** ion concentration of 0·02 $mol1^{-1}$?

2a. Primary standards [experiment 2 – Part A]

The solution of accurately known concentration is called a **standard solution**. A standard solution can only be prepared from a **primary standard**. A primary standard is a substance that is readily available and has the following characteristics:

- available in high purity (> 99.9%)
- stable in air and in solution
- a reasonably high formula mass
- is readily soluble (usually in water).

The first three characteristics are required to ensure that what is weighed out accurately is the exact weight of a substance. The most important characteristic is the standard's stability in air.

Many common substances are not stable, e.g. NaOH absorbs both water (it is both hygroscopic and deliquescent) and carbon dioxide from the air, and therefore cannot be used as a primary standard.

The common **primary standards** are oxalic acid and anhydrous sodium carbonate for acid/base titrations, ethylenediaminetetraacetic acid disodium salt (EDTA) for complexometric titrations and potassium iodate (KIO_3) for redox titrations. Other substances suitable for use as a primary standard are listed below -

- oxalic acid, $H_2C_2O_4.2H_2O$
- potassium hydrogen phthalate, $KH(C_8H_4O_4)$
- silver nitrate, $AgNO_3$
- potassium dichromate, $K_2Cr_2O_7$

2a. Primary standards

Write a brief note in your theory jotter

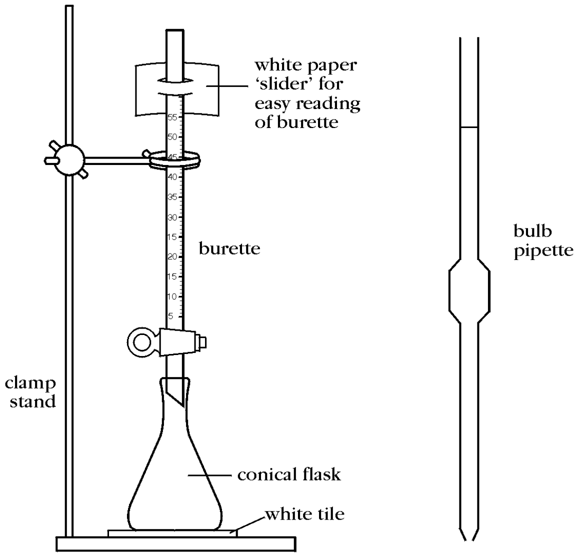
- What is meant by a **standard** solution?
- What are the **four characteristics** that are essential for a substance to be used as a **primary standard**?
- What **substances** are suitable for use as primary standards?
- Why is sodium hydroxide **unsuitable** for this purpose?
- Describe, **briefly**, the steps used to **prepare a standard solution**

2b. Titrations

A reaction where a solution of accurately known concentration is used to determine the concentration of another solution is called a **titration**.

There are three main types of titration:
- acid/base,
- complexometric and
- redox.

To carry out a titration, one solution must be prepared accurately using a **standard flask**, and the volumes must be measured accurately using a **pipette** or **burette**. All of these pieces of glass apparatus have been used in National 5 and Higher Chemistry courses.



Once a standard solution has been prepared it can be used to react (is titrated) with a known volume of solution of unknown concentration. The point at which the reaction is just complete is called the **equivalence point**. An equivalence point must be observed either by a colour change in the reaction at the equivalence point or by the addition of an indicator that changes colour at the equivalence point. This colour change happens when a certain volume of solution has been added and what is called the **end-point** of the titration is reached.

Method for carrying out a titration

The burette is set up vertically as shown in the diagram above and, after rinsing it with the solution, it is filled and the top reading recorded. The solution used is usually the standard solution.

A pipette is rinsed with the other solution and a known volume put in the conical flask. A **few** drops of indicator are added if required. The standard solution from the burette is run into the unknown solution while continuously swirling the flask.

As the end-point is approached (usually detected by a slight, transient colour change) the solution in the burette is added drop-wise until the indicator shows a permanent colour change. At the end-point the reading on the burette is taken again. Subtraction of the first reading from the second reading gives the **titre**.

It is normal to carry out one rough titration and then two accurate titrations, which must be **concordant** (i.e. agree to within +/- 0.1 cm^3). The two accurate titrations are then averaged to give the value used in the calculation. The conical flask may be placed on a white tile (or sheet of paper) to make the end-point easier to see and the burette jet must be just inside the flask at all times to avoid missing the flask during swirling.

2b. Titrations

Write a brief note in your theory jotter

- What is the purpose of carrying out a titration?
- What is meant by the **equivalence point** of a reaction?
- What is meant by the **end point** of a titration?
- What is meant by a **concordant** titration?

2c. Acid/base titrations [experiment 2 – Part C]

Acid/base titrations are called neutralisation reactions and an indicator is always required, e.g. phenolphthalein or methyl orange. The choice of indicator is important as the pH range in which it changes is critical.

Name of indicator	pH of colour change	Colour (Acid)	Colour (Base)
Methyl orange	3.0–4.4	Orange	Yellow
Methyl red	4.2–6.3	Red	Yellow
Bromothymol blue	6.0–7.6	Yellow	Blue
Phenolphthalein	8.0–9.8	Colourless	Pink

2c. Acid/base titrations

Write a brief note in your theory jotter

- How can the end point of a reaction be **determined** in a neutralisation reaction?
- What influences the **choice** of a pH indicator?

Exercise I – Acid/Base titration problems

1. 25.0 cm^3 of 0.4 moll^{-1} potassium hydroxide solution was neutralised completely by 15.5 cm^3 of sulphuric acid solution.

   What was the concentration of the acid?

2. 20.0 cm^3 of 0.25 moll^{-1} hydrochloric acid solution was neutralised completely by 13.2 cm^3 of sodium carbonate solution.

   What was the concentration of the sodium carbonate?

3. 10.0 cm^3 of 0.75 moll^{-1} sulphuric acid solution was neutralised completely by 11.7 cm^3 of sodium hydroxide solution.

   What was the concentration of the sodium hydroxide?

4. The dicarboxylic acid, oxalic acid, has molecular formula $H_2C_2O_4$.

   The equation for the reaction between oxalic acid solution and sodium hydroxide solution is

$$H_2C_2O_4(aq) + 2NaOH(aq) \longrightarrow Na_2C_2O_4(aq) + 2H_2O(l)$$

   A student used a standard solution of 0·050 moll^{-1} oxalic acid to standardise 25·0 cm^3 of approximately 0·1 moll^{-1} sodium hydroxide solution.

   The raw results for the titration are given in the table.

	1st attempt	2nd attempt	3rd attempt
Final burette reading/cm^3	19·9	38·5	18·8
Initial burette reading/cm^3	0·0	19.9	0·1
Titre/cm^3	19·9	18·6	18·7

   Calculate the actual concentration of the sodium hydroxide solution.

Experiment 2: Analysis of vinegar by titration

Aim: to determine the ethanoic acid concentration of vinegar

Introduction

Vinegar is a dilute solution of ethanoic acid and the aim of this experiment is to determine the concentration of ethanoic acid in a given sample of white vinegar by titration against **standardised** sodium hydroxide solution.

Sodium hydroxide is not a primary standard and so a standard solution of it cannot be prepared directly from the solid. A solution of approximate concentration is to be prepared and its exact concentration determined by titrating it against an acid of accurately known concentration using a suitable indicator.

A **standard** solution is one of accurately known concentration and can be prepared directly from a primary standard which, in this case, is hydrated oxalic acid, $(COOH)_2.2H_2O$ (RFM = 126.1).

Part A: Preparation of a standard solution of 0.1 moll^{-1} oxalic acid

Requirements

balance (accurate to 0.01 g)	250 cm^3 beaker	wash bottle	glass stirring rod
weighing bottle	250 cm^3 standard flask	dropper	filter funnel

oxalic acid AnalaR, $(COOH)_2.2H_2O$

deionised water

Safety

Wear eye protection and if any chemical splashes on the skin, wash it off immediately.

Oxalic acid is harmful if ingested and irritates the eyes and skin. Wear gloves.

Procedure

1. Transfer ***approximately*** 3.2 g of oxalic acid crystals to the weighing bottle and weigh ***accurately***.
2. Pour the oxalic acid crystals into a clean beaker containing about 50 cm^3 of deionised water and reweigh accurately the weighing bottle and any remaining crystals.
3. Stir the solution until all the oxalic acid dissolves and then transfer it to a 250 cm^3 standard flask.
4. Rinse the beaker several times with deionised water and add all the rinsings to the flask.
5. Make up the solution to the graduation mark with deionised water.
6. Stopper the flask and invert it several times to ensure the contents are completely mixed.

Experiment 2: Analysis of vinegar by titration

Write a brief note in your lab book

- Write the overall **aim** for the experiment.
- **Calculate** the concentration of the oxalic acid solution using the exact mass of the oxalic acid transferred to the beaker in step 2 (approximately 0.1 moll^{-1}).

Part B: Standardisation of approximately 0.1 moll^{-1} sodium hydroxide

Introduction - A sodium hydroxide solution is standardised against a standard oxalic acid solution. The stoichiometric equation for the titration reaction is:

$$(COOH)_2 + 2NaOH \rightarrow 2H_2O + (COONa)_2$$

Requirements

50 cm^3 burette	10 cm^3 pipette	100 cm^3 beakers	100 cm^3 conical flasks
wash bottle	pipette filler	white tile	filter funnel

standardised oxalic acid solution (approx. 0.1 $moll^{-1}$)

sodium hydroxide solution (approx. 0.1 $moll^{-1}$)

phenolphthalein indicator

deionised water

Safety

Wear eye protection and if any chemical splashes on the skin, wash it off immediately.

0.1 $moll^{-1}$ oxalic acid irritates the eyes and skin.

0.1 $moll^{-1}$ sodium hydroxide is corrosive to the eyes and skin.

Phenolphthalein indicator solution is highly flammable and irritating to the eyes because of its ethanol content.

Procedure

1. Rinse the 10 cm^3 pipette with a little of the sodium hydroxide solution and pipette 10 cm^3 of it into a conical flask.
2. Add two or three drops of phenolphthalein indicator to the sodium hydroxide solution in the flask.
3. Rinse the 50 cm^3 burette, including the tip, with the oxalic acid solution and fill it with the same solution.
4. Titrate the sodium hydroxide solution with the oxalic acid solution from the burette until the end-point is reached. This is indicated by the disappearance of a pink colour.
5. Repeat the titrations until two concordant results are obtained.

Experiment 2: Analysis of vinegar by titration

Write a brief note in your lab book

- Write the balanced equation for the reaction of oxalic acid with sodium hydroxide
- Record your raw data in a suitable **table** including **units** and **headings**
- **Calculate** the concentration of the sodium hydroxide solution.

Part C: Determination of the ethanoic acid content of white vinegar

Introduction - The stoichiometric equation for the titration reaction is:

$$CH_3COOH + NaOH \rightarrow H_2O + CH_3COONa$$

Requirements

50 cm^3 burette	25 cm^3 pipette	100 cm^3 beakers	100 cm^3 conical flasks
250 cm^3 standard flask	wash bottle	pipette filler	dropper
white tile	filter funnel		

white vinegar

standardised sodium hydroxide solution (approx. 0.1 moll^{-1})

phenolphthalein indicator

deionised water

Safety

Wear eye protection and if any chemical splashes on the skin, wash it off immediately.

Vinegar irritates the eyes and skin.

0.1 moll^{-1} sodium hydroxide is corrosive to the eyes and skin.

Phenolphthalein indicator solution is highly flammable and irritating to the eyes because of its ethanol content.

Procedure

1. Rinse the 25 cm^3 pipette with a little of the vinegar.
2. Dilute the sample of vinegar by pipetting 25 cm^3 of it into a clean 250 cm^3 standard flask and making it up to the graduation mark with deionised water.
3. Stopper the standard flask and invert it several times to ensure the contents are thoroughly mixed.
4. Rinse the 25 cm^3 pipette with a little of the sodium hydroxide and pipette 25 cm^3 of it into a conical flask. Add two or three drops of phenolphthalein indicator to the sodium hydroxide in the conical flask.
5. Rinse the 50 cm^3 burette, including the tip, with the diluted vinegar solution and fill it with the same solution.

6. Titrate the sodium hydroxide solution with the diluted vinegar solution from the burette until the end-point is reached. This is indicated by the disappearance of a pink colour.
7. Repeat the titrations until two concordant results are obtained.

Experiment 2: Analysis of vinegar by titration

Write a brief note in your lab book

- Write the balanced equation for the reaction of ethanoic acid with sodium hydroxide
- Record your raw data in a suitable **table** including **units** and **headings**
- **Calculate** the concentration of the ethanoic acid in the diluted vinegar and hence in the undiluted vinegar.

Weighing techniques

Write a brief note in your theory jotter

- Explain what is meant by **weighing approximately 3.2 grams accurately.**

A. Uncertainties

A1. Accuracy and precision

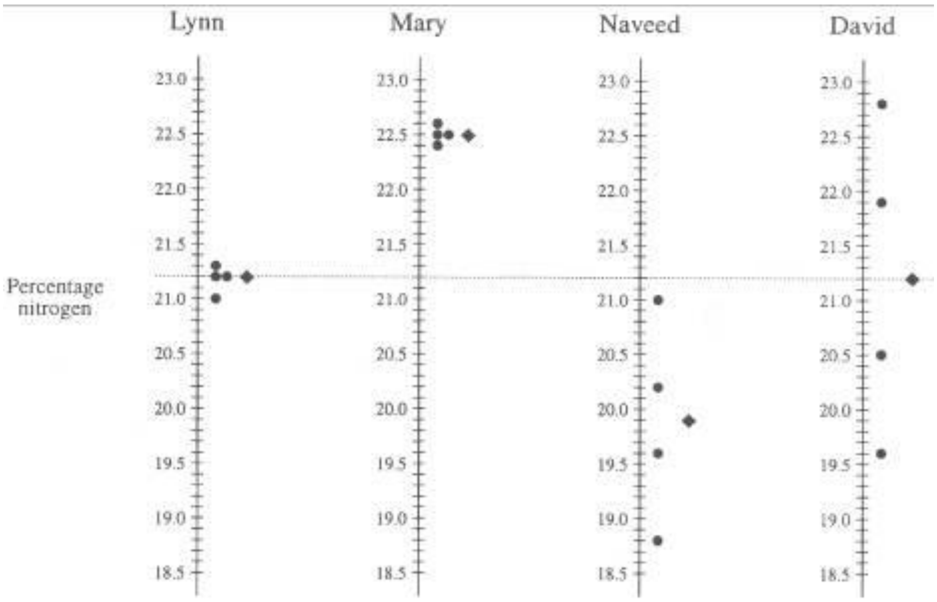
An **accurate** measurement or result is defined as one that is in close agreement with the true or accepted value.

Precise measurements or results are those that are in close agreement with each other.

Four students analysed samples of anhydrous ammonium sulfate to determine the % by mass of nitrogen four times. Their results are shown below:

Student	Lynn	Mary	Naveed	David
Percentage nitrogen	21.3	22.5	20.2	21.9
	21.2	22.4	19.6	19.6
	21.0	22.6	21.0	22.8
	21.2	22.5	18.8	20.5
Average value	21.2	22.5	19.9	21.2

These results are presented in a pictorial fashion below:



- black dots = the individual results
- ◆ black diamonds = the average values.

dotted line shows the true value for the % by mass of nitrogen in anhydrous ammonium sulfate, 21.2%.

Lynn’s results are clustered together and in close agreement with one another, they are **precise**.

All of Lynn’s results are **accurate** since they deviate only slightly from the true value.

A1. Accuracy and precision

Write a brief note in your theory jotter

- What is meant by saying that a measurement is **accurate**?
- What is meant by saying that a measurement is **precise**?
- Comment on the **precision** of the results obtained by Mary, David and Naveed.
- Comment on the **accuracy** of the results obtained by Mary, David and Naveed.

Repeatability and reproducibility

When an analyst obtains a set of results by repeating the same analytical procedure and these results are in close agreement, the results as not only being precise but **repeatable**. The procedure used can also be described as repeatable.

If a second analyst carries out the same analytical procedure and gains a set of results which are precise and close to those obtained by the first analyst, then we can describe both the results and the procedure as **reproducible**.

Lynn’s results are precise and so must be repeatable but they don’t agree with Mary’s results and so they cannot be described as reproducible.

A1. Accuracy and precision

Write a brief note in your theory jotter

- What is meant by saying that a measurement is **repeatable?**
- What is meant by saying that a measurement is **reproducible?**

A2. Quantifying errors

A convenient method is to define errors in terms of the tolerance of the piece of equipment used to make a measurement.

A 25 cm^3 class B pipette, has a tolerance of ± 0.06 cm^3, i.e. 25.00 ± 0.06 cm^3 - meaning the volume of liquid it delivers will lie between a lower limit of 24.94 cm^3 and an upper limit of 25.06 cm^3, provided the correct procedure is employed.

Balances

Readability	Uncertainty value
to 1 decimal place	±0.1 g
to 2 decimal places	±0.01 g
to 3 decimal places	±0.001 g

Pipettes

Capacity	Uncertainty value	
	Class A	Class B
10 cm^3	±0.02 cm^3	±0.04 cm^3
20 cm^3	±0.03 cm^3	±0.06 cm^3
25 cm^3	±0.03 cm^3	±0.06 cm^3
50 cm^3	±0.05 cm^3	±0.10 cm^3
100 cm^3	±0.08 cm^3	±0.15 cm^3

Burettes

Capacity	Uncertainty value	
	Class A	Class B
10 cm^3	±0.01 cm^3	±0.02 cm^3
25 cm^3	±0.03 cm^3	±0.05 cm^3
50 cm^3	±0.05 cm^3	±0.10 cm^3

Standard (or volumetric) flasks

Capacity	Uncertainty value	
	Class A	Class B
50 cm^3	±0.06 cm^3	±0.12 cm^3
100 cm^3	±0.10 cm^3	±0.20 cm^3
250 cm^3	±0.15 cm^3	±0.30 cm^3
500 cm^3	±0.25 cm^3	±0.50 cm^3
1000 cm^3	±0.40 cm^3	±0.80 cm^3

The uncertainty values quoted for burettes are in the volumes delivered by the burettes. For example, a 50 cm^3 class B burette giving a titre volume of 24.60 cm^3 has an uncertainty in this volume of ±0.10 cm^3.

A3. Absolute uncertainties and percentage uncertainties

The **absolute uncertainty** in a measurement is another way of describing its actual uncertainty. E.g. the volume contained in a 250 cm^3 class B standard flask has an actual uncertainty of ±0.30 cm^3 and so its absolute uncertainty = ± 0.30 cm^3.

The **percentage uncertainty** in a measurement is defined as:

$$\text{percentage uncertainty} = \frac{\text{absolute uncertainty}}{\text{measurement}} \times 100$$

The percentage uncertainty in the volume contained in a 250 cm^3 class B standard flask is:

$$\frac{0.30}{250.00} \times 100 = 0.12\%$$

Given the percentage uncertainty in a measurement, we can calculate its absolute uncertainty by rearranging the above expression:

$$\text{absolute uncertainty} = \frac{\text{percentage uncertainty}}{100} \times \text{measurement}$$

E.g. a solution of 0.206 moll^{-1} sodium hydroxide has a percentage uncertainty in its concentration = 1.6%. The absolute uncertainty in the concentration will be given by:

$$\frac{1.6}{100} \times 0.206 = 0.0033 \text{ moll}^{-1}$$

So, the sodium hydroxide concentration = 0.206±0.003 moll^{-1}.

Exercise J - Absolute and percentage uncertainties

1. What is the percentage uncertainty in

a) class A 10 cm^3 pipette

b) class B 10 cm^3 pipette

c) class B 50 cm^3 pipette

d) class B 100 cm^3 pipette

e) class A 50 cm^3 volumetric flask

f) titre volume of 12.3 cm^3 (50 cm^3 class B burette)

g) titre volume of 4.3 cm^3 (50 cm^3 class B burette)

2. A solution of 0.460 moll^{-1} potassium permanganate has a percentage uncertainty in its concentration = 1.1%. Calculate the absolute uncertainty and show the range in the concentration.

3. A solution of 1.960 moll^{-1} potassium hydroxide has a percentage uncertainty in its concentration = 2.3%. Calculate the absolute uncertainty and show the range in the concentration.

4. A solution of 1.200 moll^{-1} e.d.t.a. has a percentage uncertainty in its concentration = 1.9%. Calculate the absolute uncertainty and show the range in the concentration.

Experiment 2: Analysis of vinegar by titration

Write a brief note in your lab book

- **Calculate** the **absolute uncertainty** in the concentration of oxalic acid, if the percentage error is 0.3%. Show your working.

A4. Combining uncertainties

Normally in an analytical experiment we make a number of measurements and from these we calculate a final result. So how we combine the uncertainties in the individual measurements to work out the overall uncertainty in the final result depends on the mathematical operations involved in calculating the results.

Addition and subtraction

For calculations involving addition and/or subtraction, we use the absolute uncertainties in the individual measurements and simply add them to obtain the overall absolute uncertainty.

Hence for the calculation, $y = a + b - c$

the absolute uncertainty in y is given by: $u_a + u_b + u_c$

where u_a, u_b and u_c are the absolute uncertainties in the individual measurements.

Worked example 1

Mass of weighing bottle + sodium chloride = 18.54 g

Mass of weighing bottle = 12.32 g

From these data, calculate the absolute uncertainty in the mass of sodium chloride transferred from the bottle.

A balance reading to two decimal places has been used and absolute uncertainty associated with each of the mass readings must be 0.01 g.

The mass of sodium chloride transferred from the weighing bottle is 6.22 g and since the mathematical operation used to derive this result was a subtraction, then

overall absolute uncertainty = 0.01 + 0.01 = 0.02 g

Hence, the mass of sodium chloride transferred = 6.22 ± 0.02 g

Experiment 2: Analysis of vinegar by titration

Write a brief note in your lab book

- **Record** the mass of oxalic acid used in preparing your standard solution **including** the uncertainty associated with the measurement.

Multiplication and division

For calculations involving multiplication and/or division, we use the percentage uncertainties in the individual measurements. These are again added to give the overall percentage uncertainty in the final result.

Hence, for the calculation, $y = \frac{a \times b}{c}$

the percentage uncertainty in y is given by: $\%u_a + \%u_b + \%u_c$

where $\%u_a$, $\%u_b$ and $\%u_c$ are the percentage uncertainties in the individual measurements.

Worked example 2

Using a class B pipette, 25.0 cm^3 of 0.956 $moll^{-1}$ hydrochloric acid was transferred into a 500 cm^3 class B standard flask. The solution was made up to the graduation mark with deionised water. (The absolute uncertainty in the concentration of the undiluted acid is ±0.005 $moll^{-1}$)

The concentration of the diluted acid and its absolute uncertainty can be found as shown

Concentration of diluted acid $= \frac{n}{V}$

$$= \frac{\text{concentration of undiluted acid} \times \text{volume of undiluted acid}}{\text{volume of diluted acid}}$$

$$= \frac{0.956 \times 0.0250}{0.500}$$

$= 0.0478\ moll^{-1}$

In this case the calculation of the result involves multiplication and division.

So to calculate the absolute uncertainty in the concentration of the diluted acid we need first to work out the percentage uncertainty in each of the three individual measurements:

1. uncertainty in concentration of undiluted acid

absolute uncertainty in concentration of undiluted acid $= 0.005\ moll^{-1}$

percentage uncertainty in concentration of undiluted acid $= \frac{0.005}{0.956} \times 100 = 0.52\%$

2. uncertainty in volume of undiluted acid

The absolute uncertainty in a 25 cm^3 class B pipette is 0.06 cm^3.

absolute uncertainty in volume of undiluted acid = 0.06 cm^3

percentage uncertainty in volume of undiluted acid = $\frac{0.06}{25.00} \times 100 = 0.24\%$

3. uncertainty in volume of diluted acid

The absolute uncertainty in a 500 cm^3 class B standard flask is 0.50 cm^3.

absolute uncertainty in volume of diluted acid = 0.50 cm^3

percentage uncertainty in volume of diluted acid = $\frac{0.50}{500.00} \times 100 = 0.10\%$

The overall percentage uncertainty in the concentration of the diluted hydrochloric acid is gained by summing those individual percentage uncertainties that we have just calculated:

percentage uncertainty in concentration of diluted acid = 0.52 + 0.24 + 0.10

= 0.86%

absolute uncertainty in concentration of diluted acid = $\frac{0.86}{100} \times 0.0478$

= 0.00041 moll^{-1}

Hence, concentration of the diluted hydrochloric acid = 0.0478 ± 0.0004 moll^{-1}.

Experiment 2: Analysis of vinegar by titration

Write a brief note in your lab book

- **Calculate** the absolute uncertainty in the concentration of the vinegar.

Other sources of uncertainties

detecting the end-point of a titration

Judging the point at which the indicator just changes colour can be difficult to judge. We ought to be able to estimate the end-point in a titration to within one drop and since the average volume of a drop is 0.05 cm^3 then the absolute uncertainty in estimating the end-point will be ±0.05 cm^3. Suppose a 50 cm^3 class A burette was used in a titration and a titre volume was 23.2 cm^3 was obtained. There are two uncertainties associated with this titre volume: one arising from the burette itself, namely ±0.05 cm^3, and the other in estimating the end-point, namely ±0.05 cm^3.

So, overall absolute uncertainty in the titre volume = 0.05 + 0.05 = 0.10 cm^3

Hence, titre volume = 23.2 ± 0.1 cm^3

Since the two individual uncertainties are of equal magnitude, that due to estimating the end-point (±0.05 cm^3) is obviously significant and cannot be ignored.

Even if a 50 cm^3 class B burette – with an uncertainty of ±0.10 cm^3 – had been used, the uncertainty in estimating the end-point (±0.05 cm^3) would still be a major contributor to the overall uncertainty in the titre volume.

The end-points of some titrations, eg EDTA titrations, are notoriously difficult to judge and in these cases we would be justified in using ± 0.10 cm^3 rather than ± 0.05 cm^3 as the uncertainty in estimating the end-point.

Uncertainties

Write a brief note in your theory jotter

- What is are the principal sources of uncertainty in an analytical experiment that lead to a reduction in the accuracy of the measurements?

Experiment 3: Analysis of marble chips by back titration

Aim: to determine the % by mass of calcium carbonate in a sample of marble chips

Introduction

Marble (calcium carbonate) is insoluble in water and so the calcium carbonate content has to be determined by a **back titration** technique. This involves treating a sample of marble of accurately known mass with a definite amount of hydrochloric acid, i.e. the volume and concentration of the acid sample must be known accurately. An excess of acid is used and the amount remaining after neutralising the calcium carbonate is determined by titrating it against a standard solution of sodium hydroxide.

Part A: Preparation of a standard solution of 0.1 $moll^{-1}$ sodium carbonate

Introduction

A **standard** solution is one of accurately known concentration and can be prepared directly from a primary standard, in this case *anhydrous* sodium carbonate, Na_2CO_3 (RFM = 106.0).

Requirements

balance (accurate to 0.01 g)	evaporating basin	desiccator	weighing bottle
250 cm^3 beaker	250 cm^3 standard flask	wash bottle	dropper
glass stirring rod	filter funnel	Bunsen burner,	heating mat and tripod

anhydrous sodium carbonate (AnalaR)　　　deionised water

Safety

Wear eye protection and if any chemical splashes on the skin, wash it off immediately.

Sodium carbonate powder is harmful if inhaled and irritates the eyes.

Procedure

1. Heat gently and with constant stirring, approximately 10 g of anhydrous sodium carbonate in an evaporating basin, for about 15 minutes.
2. Place the evaporating basin and contents in a desiccator.
3. After cooling, weigh the evaporating basin and contents.
4. Heat the sodium carbonate again for about 5 minutes, allow to cool in the desiccator and reweigh. Repeat this process until the mass is constant.
5. Transfer approximately 2.65 g of the dried anhydrous sodium carbonate to the weighing bottle and weigh accurately.
6. Add the anhydrous sodium carbonate to a clean beaker containing about 50 cm^3 of deionised water and reweigh accurately the weighing bottle and any remaining powder.
7. Stir the solution until all the sodium carbonate dissolves and then transfer it to a 250 cm^3 standard flask.

8. Rinse the beaker several times with deionised water and add all the rinsings to the flask.
9. Make up the solution to the graduation mark with deionised water.
10. Stopper the flask and invert it several times to ensure the contents are completely mixed.

Experiment 3: Analysis of marble chips by back titration

Write a brief note in your lab book

- Write the **aim** for your experiment in your lab book
- Record your raw data in a suitable **table** including **units** and **headings**
- **Calculate** the concentration of the sodium carbonate solution using the exact mass of the anhydrous sodium carbonate transferred to the beaker in step 6 (approximately 0.1 moll^{-1})

Part B: Standardisation of approximately 1 moll^{-1} hydrochloric acid

Introduction

Hydrochloric acid is not a primary standard and so a standard solution of it cannot be prepared directly.

Approximately 1 moll^{-1} hydrochloric acid is to be diluted and then standardised against the 0.1 moll^{-1} sodium carbonate solution.

The stoichiometric equation for the titration reaction is:

$$Na_2CO_3 + 2HCl \rightarrow H_2O + CO_2 + 2NaCl$$

Requirements

100 cm^3 conical flasks	10 cm^3 and 25 cm^3 pipettes	100 cm^3 beakers	250 cm^3 standard flask
	wash bottle	pipette filler	dropper
white tile	filter funnel	50 cm^3 burette	

standardised sodium carbonate solution (approx. 0.1 moll^{-1})

hydrochloric acid (approx. 1 moll^{-1})

screened methyl orange indicator (or any other suitable indicator)

deionised water

Safety

Wear eye protection and if any chemical splashes on the skin, wash it off immediately.

1 moll^{-1} hydrochloric acid irritates the eyes and skin.

Procedure

1. Rinse the 25 cm^3 pipette with a little of the 1 moll^{-1} hydrochloric acid solution.
2. Dilute the sample of hydrochloric acid by pipetting 25 cm^3 of it into a clean 250 cm^3 standard flask and making it up to the graduation mark with deionised water.
3. Stopper the standard flask and invert it several times to ensure the contents are thoroughly mixed.
4. Rinse the 10 cm^3 pipette with a little of the sodium carbonate solution and pipette 10 cm^3 of it into a conical flask.
5. Add two or three drops of screened methyl orange indicator to the sodium carbonate solution in the flask.
6. Rinse the 50 cm^3 burette, including the tip, with the diluted hydrochloric acid and fill it with the same solution.
7. Titrate the sodium carbonate solution with the diluted hydrochloric acid from the burette until the end-point is reached. This is indicated by a green to mauve colour change.
8. Repeat the titrations until two concordant results are obtained.

Experiment 3: Analysis of marble chips by back titration

Write a brief note in your lab book

- Record your raw data in a suitable **table** including **units** and **headings**
- **Calculate** the concentration of the diluted hydrochloric acid and hence the undiluted hydrochloric acid.

Part C: Determination of the purity of marble by back titration

Requirements

250 cm^3 standard flask	marble chips	100 cm^3 glass beakers	25 cm^3 pipette
100 cm^3 conical flasks	50 cm^3 pipette	weighing bottle	balance (+/- 0.01 g)
50 cm^3 burette	wash bottle	pipette filler	white tile
dropper	filter funnel		

standardised 1.0 $moll^{-1}$ hydrochloric acid

standardised 0.1 $moll^{-1}$ sodium hydroxide

screened methyl orange indicator (or any other suitable indicator)

deionised water

Safety

Wear eye protection and if any chemical splashes on the skin, wash it off immediately.

Both 1.0 $moll^{-1}$ hydrochloric acid and 0.1 $moll^{-1}$ sodium hydroxide irritate the eyes and skin.

Procedure

1. Transfer approximately 1.0 g of marble chips to a weighing bottle and weigh the bottle and contents.
2. Transfer the marble chips to the 250 cm^3 standard flask and reweigh the bottle.
3. Rinse the 50 cm^3 pipette with a little of the 1 $moll^{-1}$ hydrochloric acid and pipette 50 cm^3 of it into the standard flask.
4. When effervescence has stopped, make up the solution in the flask to the graduation mark with deionised water.
5. Stopper the standard flask and invert it several times to ensure the contents are thoroughly mixed.
6. Rinse the 50 cm^3 burette, including the tip, with the 0.1 $moll^{-1}$ sodium hydroxide solution and fill it.

7. Rinse the 25 cm^3 pipette with some of the 'standard flask' solution and pipette 25 cm^3 of this solution into a conical flask.
8. Add two or three drops of screened methyl orange indicator to the solution in the flask.
9. Titrate the 'standard flask' solution with the sodium hydroxide solution from the burette until the end-point is reached. This is indicated by a mauve to green colour change.
10. Repeat the titrations until two concordant results are obtained.

Experiment 3: Analysis of marble chips by back titration

Write a brief note in your lab book

- Record your raw data in a suitable **table** including **units** and **headings**
- **Calculate** the percentage by mass of calcium carbonate in the marble sample using the accurate concentrations of the hydrochloric acid and sodium hydroxide solutions.

Experiment 3: Analysis of marble chips by back titration

Write a brief note in your theory jotter

- Write a brief description of the principles of **"back titration"**

2d. Redox titrations

Redox titrations are based on redox reactions. Potassium manganate(VII) (potassium permanganate) is widely used in redox titrations since it acts as its own indicator. It is decolourised in a redox reaction and therefore the end-point occurs when a very pale pink colour (slight excess of manganate(VII)) is observed.

One problem with manganate(VII) titrations is that the meniscus in the burette is often difficult to read because of the intense dark colour of the solution, but this is overcome by reading the scale at the top of the meniscus rather than the bottom.

Exercise K – Redox titration problems

1. 20.0 cm^3 of 0.015 $moll^{-1}$ potassium permanganate was acidified and added to an excess of potassium iodide solution. The iodine liberated was titrated against 0.10 $moll^{-1}$ sodium thiosulfate solution using starch indicator.

   The following half-equations will help you:

   $$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

   $$2I^- \longrightarrow I_2 + 2e^-$$

   $$2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e^-$$

   What volume, in cm^3, of sodium thiosulfate was required?

2. Alcohol levels in blood can be determined by a redox titration with potassium dichromate according to the balanced equation:

   $C_2H_5OH(aq) + 2Cr_2O_7^{2-}(aq) + 16H^+(aq) \rightarrow 2CO_2(g) + 4Cr^{3+}(aq) + 11H_2O(l)$

   What is the blood alcohol level, in $moll^{-1}$, if 9.13 cm^3 of 0.045 $moll^{-1}$ $K_2Cr_2O_7$ is required for titration of a 10.0 cm^3 sample of blood?

3. Titration with solutions of potassium bromate ($KBrO_3$) can be used to determine the concentration of arsenic.

   The balanced equation is:

   $$3H_3AsO_3 + BrO_3^- \rightarrow Br^- + 3H_3AsO_4$$

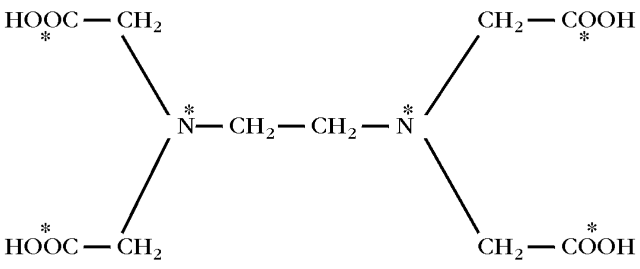
   What is the concentration of As^{3+} ions in a solution if 18.75 cm^3 of 0.130 $moll^{-1}$ $KBrO_3$ is needed to titrate 50.00 ml of the As(III) solution?

2e. Complexometric titrations [experiment 4]

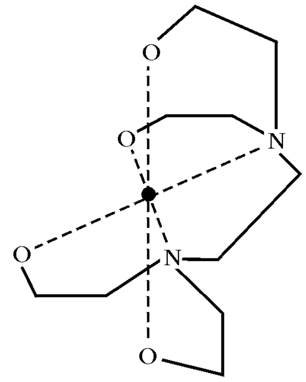
Complexometric titrations are based on the formation of a coloured **complex** by a transition metal ion.

A transition metal complex consists of a central metal ion surrounded by **ligands**. A ligand is a molecule or negative ion which bonds to the metal ion by the donation of one or more electron pairs into unfilled metal orbitals.

EDTA or ethylene diamine tetraacetic acid (shown below) is possibly the most common reagent in complexometric analysis. EDTA forms complexes with many metal ions in a one-to-one ratio.



(* attachment points through lone pairs)



Although EDTA will complex with most metal ions, the use of the reaction in analysis is limited by the availability of appropriate indicators. The indicator has to complex with the metal ion to give a visible colour that is different to that of the uncomplexed indicator.

The indicator must also bond to the metal ion less well than the EDTA molecule. This means that, as the EDTA is added, the indicator is displaced. When it is all displaced, a colour change is observed, indicating the end-point of the reaction. Murexide is an excellent indicator for calcium and nickel ions.

The theory of how such indicators work in complexometric titrations is outwith the requirements of the Advanced Higher course.

Complexometric titrations can be used to determine the concentration of metal ions, such as nickel(II), in solutions with very low concentrations (parts per million).

Example problem 3

The complexometric determination of nickel using EDTA is in two stages.

The equation for the reaction is represented by

$$Ni^{2+}(aq) \quad + \quad [EDTA]^{4-}(aq) \quad \rightarrow \quad Ni[EDTA]^{2-}(aq)$$

Stage 1 - Preparation of nickel(II) sulphate solution.

Stage 2 - Titration of the nickel(II) sulphate solution with EDTA.

In Stage 2, 20·0cm^3 of the nickel(II) sulphate solution were titrated against 0·125 moll^{-1} EDTA solution.

The results of the titrations are shown below

	rough titre	1st titre	2nd titre
initial burette reading/cm^3	0.0	18.9	0.0
final burette reading/cm^3	18.9	37.4	18.4
volume EDTA added/cm^3	18.9	18.5	18.4

The accurate mass of the nickel(II) sulphate used was 2·056 g.

Calculate the percentage by mass of nickel present in the hydrated salt from these experimental results.

Experiment 4: Complexometric titration

Aim: To determine the nickel content in a nickel(II) salt using EDTA titration

Introduction

Since EDTA forms stable complexes with most metal ions, it is widely used to determine metals in what are known as complexometric titrations. EDTA is a tetracarboxylic acid and can be represented as H_4Y. In alkaline conditions, it exists as Y^{4-} ions, which form 1:1 complexes with metal ions such as nickel(II) ions:

$$Y^{4-} + Ni^{2+} \rightarrow NiY^{2-}$$

The end-point of an EDTA complexometric titration can be detected by means of a metal ion indicator – an organic dye which changes colour when it binds with metal ions. For it to be suitable in an EDTA titration, the indicator must bind less strongly with metal ions than does EDTA. Murexide is one such indicator.

Requirements

50 cm^3 burette	20 cm^3 pipette	100 cm^3 standard flask	250 cm^3 conical flasks
weighing bottle	balance (+/- 0.01 g)	100 cm^3 beakers	25 cm^3 measuring cylinder
wash bottle	pipette filler	white tile	filter funnel
glass stirring rod			

hydrated nickel(II) sulfate ($NiSO_4.6H_2O$)	0.88 aqueous ammonia
standardised 0.10 moll^{-1} EDTA solution	deionised water

1 moll^{-1} ammonium chloride murexide indicator

Safety

Wear eye protection & immediately wash off any splashes on the skin.

Hydrated nickel(II) sulfate is harmful by ingestion and inhalation. Wear gloves.

EDTA is only toxic if ingested in large quantities.

0.88 aqueous ammonia is toxic if inhaled in high concentrations or if swallowed. The solution and vapour irritate the eyes. The solution burns the skin. Wear goggles and gloves and handle it in a fume cupboard.

1 moll^{-1} ammonium chloride is harmful and irritates the eyes.

Murexide is harmful by ingestion and if inhaled as a dust.

Procedure

1. Transfer approximately 2.6 g of hydrated nickel(II) sulfate to a weighing bottle and weigh the bottle and contents.
2. Add about 25 cm^3 of deionised water to a 100 cm^3 beaker and transfer the bulk of the nickel salt to the water.
3. Reweigh the bottle with any remaining salt.
4. Stir the mixture until the solid dissolves and transfer the resulting solution to a 100 cm^3 standard flask.
5. Rinse the beaker several times with a little deionised water and add the rinsings to the standard flask.
6. Make up the solution to the graduation mark with deionised water. Stopper the flask and invert it several times to ensure the contents are thoroughly mixed.
7. Rinse the burette, including the tip, with 0.1 moll^{-1} EDTA and fill it with the same solution.
8. Rinse the 20 cm^3 pipette with a little of the nickel salt solution and pipette 20 cm^3 of it into a conical flask. Dilute the solution to about 100 cm^3 with deionised water.
9. Add murexide indicator (approximately 0.05 g) to the diluted nickel salt solution together with approximately 10 cm^3 of ammonium chloride solution.
10. Titrate the mixture with the EDTA solution and after the addition of about 15 cm^3 make the solution alkaline by adding approximately 10 cm^3 of 0.88 aqueous ammonia (concentrated ammonia solution).

11. Continue the titration to the end-point, which is shown by the first appearance of a blue-violet colour.
    Detection of the end-point can be difficult - keep this titrated solution to help you detect end-points in subsequent titrations.

12. Repeat the titrations until two concordant results are obtained.

Experiment 4: Complexometric titration

Write a brief note in your lab book

- Record your raw data in a suitable **table** including **units** and **headings**
- **Calculate** the percentage by mass of nickel in the sample of hydrated nickel(II) sulfate using the accurate concentration of the EDTA solution provided.
- **Calculate** the theoretical percentage by mass of nickel in $NiSO_4.6H_2O$ and compare this with the experimental value. **Account for any difference**.

Exercise L – Complexometric analysis problems

1. How many moles of EDTA would be required to form a complex with the strontium ions in 25.0 cm^3 of 0.500 $moll^{-1}$ strontium chloride solution?

2. 'Hardness' in water can be caused by the presence of soluble calcium salts. If a 10.0 cm^3 sample of water required 17.00 cm^3 of 0.020 $moll^{-1}$ EDTA for complete reaction with the calcium ion present, what is its concentration in $moll^{-1}$?

Titration reactions

Write a brief note in your theory jotter

- What are the **three** main reaction types that are used for titrations?
- Why would it be undesirable to accept titration values that were **very low** (e.g. less than 6 cm^3)?
- What would you **do** about very low titre values?
- What is meant by saying that a redox reaction acts as its **own indicator**?
- Explain what is meant by a transition metal **complex**?
- What substance is commonly used in complexometric titrations?
- What **indicator** is used to detect nickel ions?

3. Skills and techniques - Colorimetry

Introduction

Colorimetry is an analytical technique used to determine the concentrations of coloured substances in solution. It relies on the fact that a coloured substance absorbs light of a colour complementary to its own and the amount of light it absorbs (absorbance) is proportional to its concentration.

A series of standard solutions of different concentrations of $KMnO_4$ is made up and the absorbance of each is measured at an appropriate wavelength (500 to 560 nm for permanganate).

Colorimetry is particularly suited to the determination of manganese in steel because the manganese can be converted into permanganate ions, which are coloured. The conversion is achieved in two stages. Using nitric acid, the managanese is first oxidised to manganese(II) ions, which are then oxidised to permanganate ions by the more powerful oxidising agent, potassium periodate.

Experiment 5: Colorimetry

Aim: To determine the % manganese in steel by colorimetry

Requirements

standard flasks ($50\ cm^3$ and $100\ cm^3$)	$50\ cm^3$ burette	wire cutters	balance (accurate to 0.001 g)
colorimeter with green filter	glass beakers ($50\ cm^3$ and $250\ cm^3$)	dropper	measuring cylinders ($50\ cm^3$ and $10\ cm^3$)
clock glass	filter funnel	tweezers	anti-bumping granules
wash bottle	optically matched cuvettes		Bunsen burner, heating mat & tripod

steel paper clips

2 mol l^{-1} nitric acid

standardised 0.0010 $moll^{-1}$ acidified potassium permanganate

85% phosphoric acid

potassium persulfate

acidified potassium periodate (5 g potassium periodate dissolved in $100\ cm^3$ of 2 mol l^{-1} nitric acid)

propanone

deionised water

Safety

Wear eye protection and if any chemical splashes on your skin wash it off immediately.

Acidified 0.0010 $moll^{-1}$ potassium permanganate is harmful if ingested and irritates the eyes and skin. Wear gloves.

2 $moll^{-1}$ nitric acid and its vapour are corrosive and toxic, causing severe burns to the eyes, digestive and respiratory systems. Wear gloves.

85% phosphoric acid is corrosive: it burns and irritates the eyes and skin. It is a systemic irritant if inhaled and if swallowed causes serious internal injury. Wear gloves.

Acidified potassium periodate solution is harmful if swallowed and is an irritant to the eyes, skin and respiratory system. It is also corrosive. Wear gloves.

Potassium persulfate is harmful if swallowed or inhaled as a dust. It irritates the eyes, skin and respiratory system, causing dermatitis and possible allergic reactions. Wear gloves.

Propanone is volatile and highly flammable, and is harmful if swallowed. The vapour irritates the eyes, skin and lungs, and is narcotic in high concentrations. Wear gloves.

Part A – Calibration graph

Procedure

1. Rinse the burette, including the tip, with 0.0010 mol l^{-1} acidified potassium permanganate and fill it with the same solution.
2. Run 2 cm^3 of the permanganate solution into a 50 cm^3 standard flask and make up to the graduation mark with deionised water.
3. Stopper the flask and invert it several times to ensure the contents are completely mixed.
4. Rinse a cuvette with some of the solution and fill it.
5. Using a colorimeter (fitted with a green filter) measure the absorbance of the solution in the cuvette. If you have more than one green filter, choose the one that gives maximum absorbance.
6. Repeat steps 2 to 5 with 6, 10 and 14 cm^3 of the permanganate stock solution in the burette.

Experiment 5: Colorimetry

Write a brief note in your lab book

- **Record** the aim of the experiment
- Summarise the **safety precautions** in a suitable table
- Collect your **raw data** in a suitable table
- Plot a **calibration graph** of ‘absorbance’ against ‘concentration of potassium permanganate’. Your teacher will provide you with the accurate concentration of the acidified potassium permanganate stock solution.

Part B – Conversion of manganese to permanganate

1. Degrease a steel paper clip by swirling it with a little propanone in a beaker. Using tweezers remove the paper clip and leave it to dry for a minute or so on a paper towel.
2. Cut the paper clip into small pieces.
3. Weigh **accurately** about 0.2 g of the paper clip pieces and transfer them to a 250 cm^3 glass beaker.
4. Add approximately 40 cm^3 of 2 $moll^{-1}$ nitric acid to the beaker and cover it with a clock glass.
5. Heat the mixture cautiously, in a fume cupboard, until the reaction starts. Continue heating gently to maintain the reaction, but remove the source of heat if the reaction becomes too vigorous.
6. Once the steel has reacted, allow the solution to cool a little. Add a couple of anti-bumping granules and then boil the solution until no more brown fumes are given off.
7. Once this solution has cooled considerably – no more than 'hand hot' – add about 5 cm^3 of 85% phosphoric acid, approximately 0.2 g of potassium persulfate and a couple of fresh anti-bumping granules. Boil the mixture for about 5 minutes.
8. To this solution, add approximately 15 cm^3 of acidified potassium periodate solution plus a couple of fresh anti-bumping granules and then gently boil the mixture. The solution will start to turn pink. Continue gently boiling until the intensity of the pink colour remains constant. This should take about 5 minutes.
9. Allow the pink solution to cool to room temperature and then transfer it to a 100 cm^3 standard flask, leaving the anti-bumping granules in the beaker.
10. Rinse the beaker several times with a little deionised water and add the rinsings (but not the anti-bumping granules) to the flask.
11. Make up the solution to the graduation mark with deionised water.
12. Stopper the flask and invert it several times to ensure the contents are completely mixed.

13. Using a colorimeter fitted with the appropriate green filter, measure the absorbance of the solution.

Experiment 5: Colorimetry

Write a brief note in your lab book

- Use your calibration graph to convert the absorbance to a permanganate concentration and then **calculate** the percentage by mass of manganese in the steel paper clip.

3. Skills and techniques - Colorimetry

Write a note in your theory jotter

- **Briefly** explain the key features of the technique of colorimetry
- Why is a wavelength of 500 to 560 nm chosen for permanganate? (What colour is permanganate solution? To what colour does 500 to 560 correspond?)

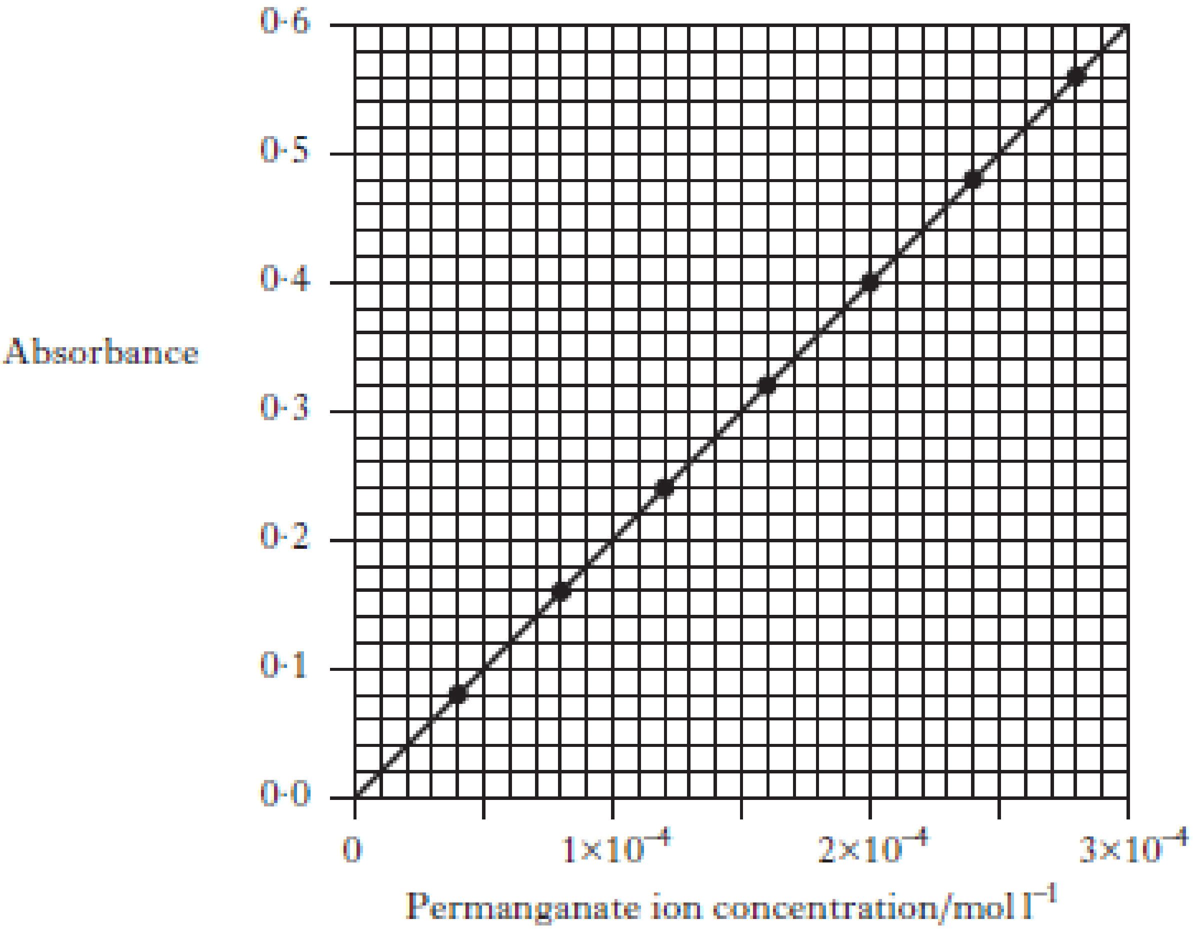
Exercise M – Colorimetry

1. The manganese content of a steel paperclip can be determined by oxidising the manganese firstly into manganese(II) ions and then to the purple permanganate ion. Colorimetry is then used to find the concentration of the permanganate ion, from which the percentage manganese in the steel paperclip can be determined.

(a) What data must be collected to allow the calibration graph to be drawn?

(b) Which colour of filter or wavelength of light should be used in this procedure?

(c) In a determination, the manganese in 0·245 g of steel was oxidised to permanganate ions and the solution made up to 100 cm^3 in a standard flask. The absorbance of the solution was measured as 0·26.



Use this information and the calibration graph to calculate the percentage of manganese in this sample of steel.

[Reference – Q4, 2013 Advanced Higher (Revised)]

Exercise N - Calculation of % yield

% yield = (quantity obtained/ quantity expected) x 100

1. Solid benzoic acid can be prepared by the hydrolysis of ethyl benzoate. The ester is heated with sodium hydroxide solution for 30 minutes.

$C_9H_{10}O_2(l) + Na^+OH^-(aq) \rightarrow C_6H_5COO^-Na^+(aq) + C_2H_5OH(l)$

gfm = 150 g

Benzoic acid is precipitated from the solution by the addition of hydrochloric acid and separated from the reaction mixture by filtration.

$C_6H_5COO^-Na^+(aq) + HCl(aq) \rightarrow C_6H_5COOH(s) + Na^+Cl^-(aq)$

gfm = 122 g

The solid benzoic acid is dried and weighed.

The results of the experiment are shown below.

Mass of flask = 52·37 g

Mass of flask + ethyl benzoate = 58·27 g

Mass of clock glass = 13·64 g

Mass of clock glass + dried solid = 17·82 g

Calculate the percentage yield of benzoic acid

2. Alkenes can be prepared from alcohols.

In an experiment, 22.56 g of cyclohexanol was dehydrated using an excess of concentrated phosphoric acid. The reaction mixture was then distilled. The crude cyclohexene was added to a separating funnel containing a solution of sodium chloride which was used to wash the cyclohexene and improve the separation of the aqueous and organic layers. The organic layer was separated and treated with anhydrous calcium chloride before it was distilled to yield 6.52 g of pure cyclohexene.

The rfm of cyclohexanol and cyclohexene are 100 and 82 respectively.

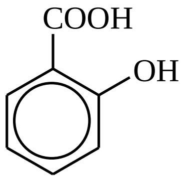
Calculate the percentage yield of cyclohexene.

Experiment 6: Preparation of an organic product

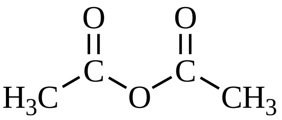
Aim: To prepare a sample of aspirin

Introduction

Aspirin (acetyl salicylic acid) is an analgesic (pain-killing), anti-inflammatory and antipyretic (fever-reducing) drug. It is an ester and can be prepared by the condensation reaction between 2-hydroxybenzoic acid (salicylic acid) and ethanoic anhydride:



2-hydroxybenzoic acid



ethanoic anhydride

After purification by recrystallisation, the product can be weighed and the percentage yield determined. The purity and identity of the final sample can be checked by measuring its melting point and mixed melting point, and by thin-layer chromatography.

Requirements

50 cm^3 conical flask	100 cm^3 conical flasks	measuring cylinders (10 cm^3 and 50 cm^3)	250 cm^3 glass beakers
thermometers	dropper	anti-bumping granules	deionised water
glass stirring rod	balance (accurate to 0.01 g)	hot plate	Buchner funnel and flask & water pump
filter papers	clock glass	oven	
melting point apparatus / capillary tubes	chromatography chamber	TLC plates	test-tubes

2-hydroxybenzoic acid

ethanoic anhydride

ice

iodine

ethyl ethanoate

85% phosphoric acid

ethanol

sample of pure aspirin

dichloromethane

Safety

Wear eye protection and if any chemical splashes on the skin, wash it off immediately.

2-Hydroxybenzoic acid is harmful by ingestion, causing nausea, vomiting etc. It is also a severe skin and eye irritant. Wear gloves.

Ethanoic anhydride is corrosive. The liquid irritates and burns the eyes and skin severely while the vapour irritates the respiratory system and may cause bronchial and lung injury. It is also flammable. Wear gloves and handle in a fume cupboard.

85% phosphoric acid is corrosive: it burns and irritates the skin and eyes. It is a systemic irritant if inhaled and if swallowed causes serious internal injury. Wear gloves.

Aspirin irritates the eyes and skin.

Ethanol is volatile, highly flammable, irritating to the eyes and intoxicating if inhaled or ingested.

Dichloromethane irritates the eyes and skin and is at its most harmful if inhaled. Wear gloves.

Ethyl ethanoate is irritating to the eyes, volatile and can irritate the respiratory system. It is highly flammable. Wear gloves.

Part A – Preparation of a sample of aspirin

1. Weigh a 50 cm^3 conical flask and to it add about 5 g of 2-hydroxybenzoic acid. Reweigh the flask and its contents.
2. In a fume cupboard, add 10 cm^3 of ethanoic anhydride from a measuring cylinder to the 2-hydroxybenzoic acid. During the addition, swirl the contents of the flask to ensure thorough mixing.
3. Add five drops of 85% phosphoric acid to the mixture, again with swirling.
4. Place the flask on a hot plate (in the fume cupboard) and heat the mixture to about 85°C. Keep it at this temperature for about 10 minutes and constantly stir the mixture.
5. Cool the mixture in an ice/water bath and then pour it into approximately 150 cm^3 of cold water contained in a 250 cm^3 beaker.
6. Filter off the precipitate at the water pump and wash it thoroughly with several portions of cold water.

7. Transfer the crude product to about 15 cm^3 of ethanol in a 100 cm^3 conical flask. Add a couple of anti-bumping granules and heat the mixture gently on a hot plate until it dissolves.
8. Pour this solution into a 100 cm^3 conical flask containing about 40 cm^3 of water. If an oil forms, reheat the mixture on a hot plate to dissolve it. If the oil persists, add a few drops of ethanol and reheat the mixture.
9. Set aside the mixture and allow it to cool to room temperature.
10. Filter off the crystals of aspirin at the water pump and wash them with a small volume of cold water. Allow air to be drawn through the crystals for a few minutes in order to partially dry them.
11. Weigh a clock glass and transfer the crystals to it. Dry the crystals in an oven at about 100°C and then reweigh the clock glass and crystals.

Part B – Determination of the melting point of the aspirin product.

12. Grind a 50:50 mixture of the product and a pure sample of aspirin and determine the mixed melting point. This will give you some indication of the purity of the aspirin you have prepared.

Part C – Determination of the purity of the aspirin product.

13. Take a TLC plate and using a pencil lightly draw a line across the plate about 1 cm from the bottom. Mark two well-spaced points on the line.
14. Place small amounts (about a third of a spatulaful) of your aspirin product and a pure sample of aspirin in two separate test-tubes.
15. Add about 1 cm^3 of solvent (a 50:50 mixture of ethanol and dichloromethane) to each of the test-tubes to dissolve the aspirin samples.
16. Use capillary tubes to spot each of the two samples onto the TLC plate. Allow to dry and repeat two or three more times.
17. After the spots have dried, place the TLC plate into the chromatography chamber, making sure that the pencil line is above the level of the solvent (ethyl ethanoate). Close the chamber and wait

until the solvent front has risen to within a few millimetres of the top of the plate.

18. Remove the plate from the chamber, immediately marking the position of the solvent front, and allow it to dry.
19. Place the TLC plate in a beaker containing a few iodine crystals and cover the beaker with a clock glass. Once any brownish spots appear, remove the plate and lightly mark the observed spots with a pencil.

3. Skills and techniques - Preparation of an organic product

Write a brief note in your theory jotter

- Describe how **recrystallisation** is carried out.
- Describe how to carry out **TLC** (include the interpretation of the results)

Experiment 6: Preparation of an organic product

Write a brief note in your lab book

- Write the **aim** of the experiment
- **Record** all masses used in a suitable manner
- **Calculate** the percentage yield of aspirin.
- **Calculate** the R_f values of the spots. This will give you some indication of the purity of the aspirin you have prepared.

4. Stoichiometric calculations

4a. Empirical formula

The **empirical formula** for a compound is the simplest ratio of the elements present. It may not actually correspond to the number of each type of atom present in a substance.

e.g. ethyne, C_2H_2, has an empirical formula of CH. The empirical formula is one found as the result of experimentation.

Example problem 4

0.875 g of a hydrocarbon is found to contain 0.75 g of carbon. What is the hydrocarbon's empirical formula?

4a. Empirical formula

Write a brief note in your theory jotter

- What is the meaning of an **empirical formula?**

Exercise O - Calculation of an Empirical formula

1. 1.224 g of an organic compound is burned completely in oxygen to form 1.87 g of carbon dioxide and 0.765 g of water. What is the compounds empirical formula?

2. The formula of potassium hydrogen oxalate can be written as $K_xH_y(C_2O_4)_z$.

In an experiment to determine the values of x, y and z, 10.25 g of this compound was dissolved in water and the solution made up to one litre.

(a) 25.0cm^3 of the solution was pipetted into a conical flask and then titrated with 0·0364 mol l^{-1} acidified potassium permanganate at 60 °C. The average titre volume was 22.0 cm^3.

The equation for the reaction taking place in the conical flask is

$$5C_2O_4{}^{2-} + 16H^+ + 2MnO_4{}^- \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

(i) What colour change would indicate the end point of the titration? 1

(ii) From the titration result, calculate the number of moles of oxalate ions, $C_2O_4{}^{2-}$, in 25.0cm^3 of the solution. 1

(iii) Calculate the mass of oxalate ions in one litre of the solution. 1

(iv) Using another analytical procedure, 10.25 g of potassium hydrogen oxalate was found to contain 0.080 g of hydrogen. 1

Use this information with the answer to (a)(iii) to calculate the mass of potassium in this sample.

(b) Calculate the values of x, y and z. 2

3. An antibiotic contains C,H,N,S and O. Combustion of 0.3442 g of the compound in excess oxygen yielded 0.528 g CO_2, 0.144 g H_2O, 0.128 g SO_2 and 0.056 g N_2. What is the antibiotic's empirical formula?

4b. Calculation of concentrations from titrations

Exercise P - Calculation of concentrations from titrations

1. The equation for the reaction between oxalic acid solution and sodium hydroxide solution is

$$H_2C_2O_4(aq) + 2NaOH(aq) \rightarrow Na_2C_2O_4(aq) + 2H_2O(l)$$

A student used a standard solution of 0·053 mol l^{-1} oxalic acid to standardise 25·0 cm^3 of approximately 0·1 mol l^{-1} sodium hydroxide solution.

The raw results for the titration are given in the table.

	1st attempt	**2nd attempt**	**3rd attempt**
Final burette reading/cm^3	22.0	43.6	22.2
Initial burette reading/cm^3	0·0	22.0	0·5
Titre/cm^3	22.0	21.6	21.7

Calculate the accurate concentration of the sodium hydroxide solution.

2. The percentage of calcium carbonate in a sample of limestone can be determined by ***back titration*** as follows:

2.00 g of limestone were dissolved in 60.0 cm^3 of 0.50 $moll^{-1}$ hydrochloric acid. After the reaction was completed, insoluble impurities were removed by filtration and the amount of unreacted acid was determined by titration with 0.10 $moll^{-1}$ sodium hydroxide solution.

15.0 cm^3 of the 0.40 $moll^{-1}$ sodium hydroxide were required to neutralise the unreacted acid.

a) Calculate the number of moles of hydrochloric acid that had reacted with the limestone.

b) Calculate the percentage (by mass) of calcium carbonate in the sample of limestone.

3. A fertiliser contains ammonium phosphate as the only source of nitrogen and phosphorus elements essential for plant growth. To determine the percentage nitrogen in the fertiliser, the following was carried out:

1.40 g of the fertiliser was weighed and then heated with 2.0 $moll^{-1}$ sodium hydroxide solution and the gas given off was absorbed in 50 cm^3 of 0.50 $moll^{-1}$ hydrochloric acid solution. When the reaction was finished, unreacted hydrochloric acid was titrated with 0.50 $moll^{-1}$ sodium hydroxide solution. 10.0cm^3 of the alkali were needed for neutralisation.

a) Name the gas given off when the fertiliser is heated with sodium hydroxide.

b) State whether high accuracy is required in measuring the volume of

i) the 2.0 $moll^{-1}$ sodium hydroxide solution

ii) the 0.50 $moll^{-1}$ hydrochloric acid solution

iii) the 0.10 $moll^{-1}$ sodium hydroxide solution

c) Write the equation for the reaction of the gas referred to in **a)** with hydrochloric acid.

d) Calculate the number of moles of hydrochloric acid which reacted with the gas.

e) Calculate the percentage (by mass) of nitrogen in the fertiliser.

Exercise P - Calculation of % purity by mass

1. In the volumetric method, a complexometric titration can be carried out.

   1·13 g of hydrated copper(II) sulfate, $CuSO_4.5H_2O$, was weighed out accurately and made up to 100·0 cm^3 in a standard flask using distilled water.

   25·0 cm^3 portions were titrated against 0·095 $moll^{-1}$ EDTA solution using murexide indicator.

   The results of the complexometric titrations are shown in the table below.

	rough titration	1st titration	2nd titration
Initial burette reading /cm^3	0·0	12.0	23.7
Final burette reading /cm^3	12.0	23.7	35.5
Volume of EDTA added /cm^3	12.0	11.7	11.8

   From the experimental results, calculate the percentage of copper, by mass, in the hydrated copper(II) sulfate sample.

2. A 1.237 g sample of a metallic alloy containing iron was dissolved in sulphuric acid and titrated with standard potassium dichromate ($K_2Cr_2O_7$) to determine its iron content.

   The equation is:

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

   The iron in the sample required 25.70 cm^3 of 0.120 $moll^{-1}$ potassium dichromate for complete oxidation. Calculate the percentage of iron in the sample.

Exercise R - Gravimetric analysis

1. Gunmetal is an alloy of mainly copper and tin. The copper content is sufficiently high to be worth recovering from gunmetal scrap. In order to determine the approximate percentage of copper in a sample, the following estimation was carried out.

0.500 g of the gunmetal sample was weighed into a beaker and 50% nitric acid solution was added. When the metal had dissolved, the solution was cooled and diluted. At this stage an insoluble tin compound was formed and this was filtered off.

Sodium carbonate was added to the filtrate and the thick, green, gelatinous precipitate was filtered, washed and dried. The green precipitate was heated strongly in a crucible until decomposition was complete and a black powder obtained.

Results:

mass of crucible + black powder = 26.658 g

mass of crucible = 26.101 g

a) Write an equation for the decomposition of the green precipitate to the black powder.

b) Calculate the percentage copper in the gunmetal alloy.

c) Copper(II) ions can also be determined by a complexometric titration method.

i) Name a suitable reagent for this method.

ii) Give one advantage and one disadvantage of this method compared with the precipitation method given above.

2a: Excess sodium carbonate was added to 50.0 cm^3 of a solution containing copper(II) ion. The precipitate of copper(II) carbonate was filtered off, washed and heated strongly to convert it to copper(II) oxide.

The equations are:

$$Cu^{2+} + CO_3^{2-} \rightarrow CuCO_3$$

$$CuCO_3 \rightarrow CuO + CO_2$$

If the copper(II) oxide weighed 0.519 g, what is the concentration of Cu^{2+} in the original solution?

2b. When sodium carbonate solution is added to aqueous copper(II) ions, the precipitate in fact consists of a mixture of copper(II) carbonate and hydroxide. Would this affect the analysis above? Give an explanation for your answer.

3a. Gold has compounds containing gold(I) ion or gold(III) ion. A sample of gold chloride was treated with a solution of silver nitrate, $AgNO_3$, to convert the chloride ion in the compound to a precipitate of AgCl. A 0.607 g sample of the gold compound gave 0.860 g of silver(I) chloride.

Calculate the percentage of chlorine in the gold compound.

3b. What is the formula of the original gold compound?

Supplementary Stoichiometry Questions

Gravimetric analysis

1: What mass of lead(II) sulfate would be precipitated from a solution containing 0.963 g of lead(II) nitrate by the addition of excess sodium sulfate?

2: One way to restore the brightness of lead pigments in old masters that have been dulled by the formation of lead sulfide is to treat with hydrogen peroxide. This converts the brown lead sulfide into white lead sulfate.

$$PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O$$

What mass in grams of hydrogen peroxide should be used to restore a picture containing 16.43 g of lead sulfide if a 10% excess is required to ensure effectiveness?

3: Excess potassium chromate was added to a solution of silver(I) nitrate to precipitate silver chromate. 25.37 g of silver chromate was produced. What mass, in grams, of silver nitrate was present in the original solution?

Solutions

1: There are only 7.5 g of copper(II) sulphate ($CuSO_4.5H_2O$) left in a bottle. What volume, to the nearest cm^3, of 0.1 $moll^{-1}$ solution could be made from this weight?

2: Hydrogen sulfide was passed into 500 ml of an acidified solution containing copper(I) ions to precipitate copper(I) sulfide. If 7.44 g of copper(I) sulfide was produced, what is the concentration of copper(I) ions in $moll^{-1}$?

Acid-Base titrations

1: 50.0 ml of 0.120 $moll^{-1}$ potassium hydroxide solution are completely neutralised by 24.4 ml of sulphuric acid.
What is the concentration of the acid in $moll^{-1}$?

2: The effluent from a chemical plant contains nitric acid. 15.0 cm^3 of the effluent requires 32.7 ml of 0.015 $moll^{-1}$ sodium hydroxide for neutralisation.
What is the concentration of the acid in $moll^{-1}$?

3: What is the concentration of citric acid (a triprotic acid) in lemon juice if 50 cm^3 of the juice require 12.0 ml of 0.250 $moll^{-1}$ sodium hydroxide solution for complete neutralisation?

4: A flask contains 52.5 cm^3 of a 0.15 $moll^{-1}$ solution of sulphuric acid. What volume of 0.35 $moll^{-1}$ sodium carbonate (Na_2CO_3) is required to react completely with the sulphuric acid?

5: An indigestion remedy (antacid) contains an aqueous suspension of magnesium hydroxide ($Mg(OH)_2$). This suspension was diluted 10 times and 25.0 cm^3 of this reacted completely with 21.9 cm^3 of 0.25 $moll^{-1}$ hydrochloric acid.

What is the concentration of magnesium hydroxide in the original suspension in $moll^{-1}$?

6: A standard solution of sodium carbonate was prepared by dissolving 5.06 g of anhydrous sodium carbonate in water and making it up to 500 cm^3. Using a pipette, 25.0 cm^3 portions of this solution were removed from the flask and titrated against hydrochloric acid giving an average titre volume of 19.2 cm^3.

Calculate the concentration of the hydrochloric acid.

Redox titrations

1: 25.0 cm^3 of a solution of sodium nitrite was acidified then titrated with 0.15 $moll^{-1}$ potassium permanganate. If 15.3 cm^3 were required for reaction and the half-equation for nitrite oxidation is:

$$NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e$$

What is the concentration of sodium nitrite, in $moll^{-1}$?

2: Ozone (O_3) reacts with iodide ions according to the equation:

$$O_3 + 2I^- + H_2O \rightarrow O_2 + I_2 + 2OH^-$$

230 litre sample of air containing ozone was passed through one litre of a solution of potassium iodide producing iodine. Samples were removed using a 10 cm^3 pipette and an average titre of 16.25 cm^3 of 0.01 $moll^{-1}$ sodium thiosulfate ($S_2O_3{}^{2-}$) was obtained.

$$I_2(aq) + 2S_2O_3{}^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6{}^{2-}(aq)$$

What mass of ozone was in the air sample?

3: Propanone reacts with iodine in alkaline solution according to the equation:

$$(CH_3)_2CO + 3I_2 + 4NaOH \rightarrow CHI_3 + 3NaI + CH_3CO_2Na + 3H_2O$$

Titration of 25.0 cm^3 of a solution of propanone required 14.65 cm^3 of 0.25 $moll^{-1}$ iodine for complete reaction. What is the concentration, in $moll^{-1}$, of propanone?

4: 18.36g of iron(II) ammonium sulphate, $Fe(NH_4)_2(SO_4)_2.6H_2O$, was dissolved in 350 cm^3 of distilled water. The solution was then diluted to 500 cm^3 using dilute sulphuric acid.

From this solution a chemist removed 25.0 cm^3 samples by pipette and these were titrated using potassium permanganate solution. An average titre of 20.2 cm^3 of the permanganate solution was required to reach the end-point at which all the iron(II) ions had been converted to iron(III) ions.

Calculate the concentration of the potassium permanganate solution.

5: 2.25 g of impure cerium(IV) oxide (CeO_2) was dissolved in sulphuric acid and made up to 500 ml. 25 cm^3 of this solution was titrated with 30.0 cm^3 of 0.02 $moll^{-1}$ ammonium iron(II) sulphate.

The ionic equation for the reaction is:

$$Ce^{4+} + Fe^{2+} \rightarrow Ce^{3+} + Fe^{3+}$$

What is the percentage purity of the original cerium(IV) oxide?

Complexometric volumetric analysis

1: How many moles of EDTA would be required to form a complex with the magnesium ions in 12.5 cm^3 of 0.80 $moll^{-1}$ magnesium sulphate solution?

2: 'Hardness' in water can be caused by the presence of soluble magnesium salts. If a 50.0 cm^3 sample of water required 13.55 cm^3 of 0.0005 $moll^{-1}$ EDTA for complete reaction with the magnesium ion present, what is its concentration in $moll^{-1}$?

3: In a titration of Co^{3+} ion with ethylene diamine, 10.0 ml of 0.050 $moll^{-1}$ Co^{3+} reacted completely with 60.0 cm^3 of 0.25 $moll^{-1}$ ethylene diamine. How many ethylene diamine molecules complex with each cobalt(III) ion?