Kirkcaldy High School

Chemistry

Advanced Higher

Unit 4 – Researching Chemistry

EXPERIMENT INSTRUCTIONS

Researching Chemistry Overview

Structure

The researching chemistry takes place in 2 parts

1. Carry out the experiments that allow you to demonstrate an understanding of the chemistry underlying various practical techniques and maintain a Lab Book to become experienced in the following skills in preparation for the investigation.

- Keeping a Lab Book for all experimental data, dated every day and checked regularly.
- Understanding underlying chemistry
- Recording all raw data in a suitable format
- Processing results clearly
- Evaluating the results with respect to their accuracy, precision and the effect of uncertainties on the conclusions you can draw
- Referencing

This assessment is carried out **through the final exam.** That is, there will be exam questions on the techniques you experience.

2. Carry out and write up an investigation. This will assess your ability to apply your understanding of underlying chemical principles to a practical investigation. You will have to

- carry out background research (keeping accurate note of your reference sources)
- write an account of the underlying chemistry
- plan your procedures
- record your results
- record all your work in a Lab Book.

This constitutes the internal assessment.
For the external part of this assessment you will write a report according to the guidance set out by SQA. This will be around 2500-4500 words long and will be worth 25 marks or 25% of the final grade.
The SQA notes are designed to show you the correct way to reference websites in your work. Note that in the text the shortened version of the url is used. At the end, the complete url is given, together with the date visited. You should get into the habit of writing references in this way – NO OTHER method is acceptable in chemistry, although there are other ways to reference as you will find out in other subjects.

Health and Safety

All the safety information is given in the instruction sheets. You are expected to comply with the health and safety advice given Wear glasses and gloves and a white lab coat.

Practical Techniques and Apparatus

Outcome 1 In order to be able to make informed choices and decisions during the planning stage of the Investigation, teachers/lecturers should ensure that candidates are familiar with the following apparatus.

- Digital balance
- Colorimeter or visible spectrophotometer
- Buchner or Hirsch or sintered glass funnel
- Glassware with ground glass joints (‘Quickfit’ or similar)
- Thin layer chromatography apparatus
- Melting point apparatus
- Separating funnel

Candidates should also be familiar with the following skills and techniques including any relevant background theory as well as having opportunities to practise them prior to undertaking the Investigation.

Skill	Experiment	Date Completed
(a) Weighing by difference and gravimetric analysis	4	
(b) Preparing a standard solution	1	
(c) Using a reference or control or blank determination	7, 8	
(d) Carrying out a complexometric titration	3	
(e) Carrying out a back titration	2	
(f) Using a colorimeter or visible spectrophotometer and carrying out dilution to prepare a calibration graph	8	
(g) Distilling	9	
(h) Refluxing	7	
(i) Using vacuum filtration methods	5, 7	
(j) Recrystallising	5, 6, 7	
(k) Determining % yield experimentally	5, 6, 7, 9	
(l) Using thin-layer chromatography	6	
(m) Using melting point apparatus and mixed melting point determination	6, 7	
(n) Using a separating funnel and solvent extraction	9	
(o) Carrying out stoichiometric calculations	1, 2, 3, 4, 5, 6, 7, 8, 9	
(p) Volumetric Analysis	1, 2, 3	
(q) Scientific Precision and Uncertainties	Project	

Stoichiometry

Understand how to use the balanced (stoichiometric) equation to calculate quantitatively the substances involved in reactions.

- Know how to use volumetric analysis to determine the accurate concentration of a substance.
- Know what is meant by a standard solution
- Know the characteristics for a primary standard
- Understand what is meant by equivalence point and ‘end point’
- Know what is meant by the terms acid/base titration, complexometric titration, redox titration
- Know what is meant by gravimetric analysis

Carrying out stoichiometric calculations

Stoichiometry is the study of quantitative relationships involved in chemical reactions. The ability to balance and interpret equations enabling calculations to be carried out involving any of the above skills/techniques is an important part of chemistry at this level and is examinable in the Course assessment.

Measurement and Associated Errors

Read the section in the practical booklet about measurement and associated errors and make notes about good practice in your day book. Refer to these points when you are evaluating your experimental work.

Experiment 1 Determination of the ethanoic acid content of Vinegar

Skills

(b) Preparing a standard solution
(o) Carrying out stoichiometric calculations
(p) Volumetric Analysis

Aim

Determine the % of ethanoic acid in a sample of vinegar

Theory

Standard Solutions

- A solution of accurately known concentration is known as a standard solution.
- A standard solution can be prepared directly from a primary standard. A primary standard must have, at least, the following characteristics:
- high state of purity
- stability in air and in solution
- solubility
- reasonably high formula mass

Examples of primary standards include

- sodium carbonate, Na_2CO_3
- oxalic acid, $H_2C_2O_4.2H_2O$
- potassium hydrogen phthalate, $KH(C_8H_4O_4)$
- silver nitrate, $AgNO_3$
- potassium iodate, $KI\ O_3$
- potassium dichromate, $K_2Cr_2O_7$

Standardising solutions

Certain compounds such as sodium hydroxide are not acceptable as primary standards. Therefore it is not possible to make up solutions whose exact concentration is known. Sodium hydroxide for example, absorbs moisture from the air, therefore a weighed mass of the solid will have an indeterminate number of moles within it.

The exact concentration of such compounds is determined by titration with a primary standard. Ttitrations should be repeated until concordant results are obtained.

Oxalic acid is used to standardise sodium hydroxide using a phenolphthalein indicator. An accurate solution of oxalic acid is made up, then used to determine the concentration of the sodium hydroxide which can then be used for titrimetric analysis. **Keep the sodium hydroxide**.

Hydrochloric acid would be standardised with sodium carbonate, using methyl orange indicator.

Part A: Preparation of Standard 0.1 mol l^{-1} Oxalic acid Solution

Oxalic acid: $(COOH)_2 .2H_2O$ - formula mass = 126 $gmol^{-1}$

For 250 cm^3 of 0.1 mol l^{-1} oxalic acid solution, the mass required is:

$$126 \times 0.1 \times 0.25 = 3.15g$$

Chemicals and Apparatus:

- Oxalic acid dihydrate (AR)
- Standard flask (250 cm^3)
- Balance (accurate to 0.01 g)
- Wash bottle/distilled water
- Specimen tube (or weighing bottle)
- Dropping pipette
- Beaker (250 cm^3)

Risk Assessment

- Oxalic acid – harmful by ingestion (LD50 0.38g/kg) and by inhalation of dust; prolonged contact causes burns and dermatitis; irritating to skin and eyes; evidence of reproduction effects. Wear eye protection and disposable gloves. Owing to the crystalline nature of the acid it is easy to avoid raising dust. Wash any splashed off the skin.

Procedure:

1. Weigh accurately by difference pure oxalic acid dihydrate (about 3.15g) into a clean, dry 250 cm^3 beaker. Record all the masses in your day book.
2. Add about 50 cm^3 distilled water, stir to dissolve and pour into a clean 250 cm^3 standard flask.
3. Wash out the beaker using distilled water, adding all washings to the flask.
4. Make up to the calibration mark with distilled water.
5. Stopper the flask and shake well to mix.
6. Calculate the exact concentration of your oxalic acid.
7. Explain the underlying chemistry
8. Write the conclusion for this experiment

Remember to write the aim, background theory, all raw data for each section, all calculations for each section, a conclusion and an evaluation for the overall experiment.

Part B: Standardisation of Approximately 0.1 mol l^{-1} Sodium Hydroxide Solution

Theory

Equation for the reaction:

$$\mathbf{2NaOH} + \mathbf{(COOH)_2.2H_2O} \rightarrow \mathbf{(COONa)_2} + \mathbf{4H_2O}$$

2 moles 1 mole

Chemicals and Apparatus:

- Standard oxalic acid solution (approximately 0.1 mol l-1)
- Sodium hydroxide solution (approximately 0.1 mol l-1)
- Phenolphthalein indicator
- Pipette (20 cm^3)
- Pipette filler
- Burette (50 cm^3)

Risk Assessment

Both 0.1 mol l^{-1} solutions of the acid and the alkali will irritate eyes. Wear eye protection, avoid skin contact and wash any splashes off the skin.

Procedure

1. Pipette the sodium hydroxide solution (20 cm^3) into a conical flask and add 2 or 3 drops of phenolphthalein solution.
2. Rinse and fill a burette with the oxalic acid solution, and note the reading on the scale.
3. Add acid to the contents of the conical flask until the indicator just begins to change.
4. Continue adding acid 1 cm^3 at a time until the solution is permanently colourless, i.e. the end-point has been reached. (Rough titre).
5. Note the burette reading.
6. Repeat several times, adding the acid dropwise as the end-point is approached. There should be 3 concordant results.
7. Calculate the exact concentration of the sodium hydroxide
8. Give the underlying chemistry to the procedure
9. Note the error in the burette, the pipette and the standard flask
10. Write the conclusion to the experiment
11. Evaluate the procedure and the results.

Part C: Determination of the ethanoic acid content of Vinegar

Theory

The equation for the reaction is:

$$\mathbf{NaOH} \quad + \quad \mathbf{CH_3.COOH} \rightarrow \quad \mathbf{CH_3\,COONa} \quad + \quad \mathbf{H_2O}$$

1 mole 1 mole

Chemicals and Apparatus

- Vinegar
- Pipette (20 cm^3)
- Standard flask (100 cm^3)
- Pipette filler
- Standard sodium hydroxide solution Burette (50 cm^3) (approximately 0.1 mol l-1)
- Conical flask (100 cm^3)
- Phenolphthalein indicator
- Wash bottle/distilled water
- Balance (accurate to 0.01g)
- Dropping pipette

Risk Assessment

Sodium hydroxide (0.1 mol l^{-1}) will irritate the eyes; wear eye protection and since the sodium hydroxide is used in the burette, lift it off the bench to keep the filling process below eye level.

Procedure

1. Weigh out accurately about 20g of vinegar into a 100 cm^3 standard flask.
2. Make up to the calibration mark with distilled water and shake.
3. Titrate 20 cm^3 portions of this solution with standard 0.1 mol l^{-1} sodium hydroxide solution (using phenolphthalein as indicator) until three concordant results are obtained (within 0.1 cm^3).
4. Calculate the exact concentration of the ethanoic acid in the vinegar
5. Calculate the mass of ethanoic acid in the 20g sample and thus the percentage by mass
6. Give the underlying chemistry to the procedure, including chemical equations.
7. Write the conclusion to the experiment
8. Evaluate the procedure and the results. If possible note the expected % of ethanoic acid from any information given on the bottle. In general the ethanoic acid concentration would be in the region of 5-6%. How close are you to the expected result? This is a measure of accuracy. What factors could contribute to the accuracy of your result?

Experiment 2 Determination of The Purity of Marble

Skills

(e) Carrying out a back titration
(o) Carrying out stoichiometric calculations
(p) Volumetric Analysis

Aim

To determine the % mass of calcium carbonate in a sample of marble.

Theory

When the substance that is being analysed is **insoluble**, it cannot be determined by direct titration.
An insoluble substance can be reacted with a known excess of a solution that can be analysed using titration (A mol). The quantity of solution that has not reacted is then determined by titration (B mol). The number of moles that have reacted with the insoluble substance is therefore (A – B mol).
Marble contains insoluble calcium carbonate. This can be reacted with excess hydrochloric acid. The unreacted hydrochloric acid can be determined by titration with sodium hydroxide. **Use the sodium hydroxide you prepared earlier.**
Determination of the purity of marble by **back titration. DO NOT MEASURE EXACTLY 1g of marble but measure accurately approximately 1g of marble e.g 1.05g or 0.98g. record the mass accurately.**
Since calcium carbonate is insoluble in water, its purity must be determined by back titration. The carbonate is first treated with excess acid (a definite volume of acid of known concentration) and the amount of excess acid is then determined by titration with a standard alkali.
Equations are:

$$\underset{\text{1 mole}}{CaCO_3} + \underset{\text{2 moles}}{2HCl} \rightarrow CaCl_2 + H_2O + CO_2$$

$$\underset{\text{1 mole}}{NaOH} + \underset{\text{1 mole}}{HCl} \rightarrow NaCl + H_2O$$

Chemicals and Apparatus

- Standard hydrochloric acid (bench – 2 mol l^{-1})
- Standard sodium hydroxide solution (approximately 0.1 mol l-1)
- Methyl orange indicator (screened)
- Marble
- Filter funnel
- Standard flask (250 cm^3)
- Pipette (20 cm^3)
- Pipette filler
- Burette (50 cm^3)
- Conical flask (100 cm^3)
- Wash bottle/distilled water
- Balance (accurate to 0.01g)
- Dropping pipette
- Specimen tube (or weighting bottle)

Risk Assessment

Sodium hydroxide (0.1 mol l^{-1}) and hydrochloric acid (2 mol l^{-1}) will both irritate the eyes; wear eye protection. Since the sodium hydroxide is used in the burette, lift the burette down off the bench to keep the filling process below eye level.

Procedure

1. Weigh accurately by difference approximately 2 g of powdered marble and transfer to a 250 cm^3 standard flask containing 50 cm^3 of 2 mol l^{-1} hydrochloric acid measured from a burette. **DO NOT MEASURE EXACTLY 2 g of marble but measure accurately approximately 2 g of marble *e.g.* 1.95g or 1.98g and record the mass accurately.**
2. When effervescence has stopped, make up to the calibration mark with distilled water and shake well.
3. Titrate 20 cm^3 portions of this solution with standard sodium hydroxide solution (0.1 mol l^{-1}) using screened methyl orange as indicator until three concordant results are obtained.
4. Calculate the number of moles of hydrochloric acid added at the start (A)
5. Calculate the number of moles of hydrochloric acid remaining (B)
6. Calculate the number of moles that reacted with the marble (A-B)
7. Calculate the number of moles of calcium carbonate and thus the mass in the marble
8. Calculate the % by mass of calcium carbonate in the marble
9. Describe the underlying chemistry, including calculations

10. Write the conclusion to the experiment
11. Evaluate the procedure.

Calculation Support

1. Calculate the number of moles of HCl added (A mol acid)
2. Calculate the number of moles of HCl remaining in a 20 cm^3 sample/aliquot of the marble/acid mixture.
3. Multiply this up to find the total number of moles remaining unreacted in the 250 cm^3 standard flask (B mol)
4. Subtract B from A to find the number of moles of acid that did react and thus the number of moles of calcium carbonate in the 1g sample.
5. Calculate the mass of calcium carbonate in the sample and then, using the accurate mass recorded earlier, calculate the % by mass.

Experiment 3   Complexometric Determination of Nickel Using EDTA

Skills

(d) Carrying out a complexometric titration
(o) Carrying out stoichiometric calculations
(p) Volumetric Analysis

Aim

To determine the % of Nickel in a salt

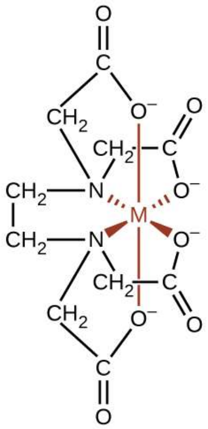
Theory

Complexometric titrations are based on reactions in which complexes are formed. EDTA is an important complexometric reagent and can be used to determine the concentration of many different metal ions in solution.

Nickel ions can form complex ions in which a positive metal ion is surrounded by ligands.

Ligands are negative ions or molecules with unbonded electrons that provide a negative centre. One theory suggests that the negative charge on the ligands is attracted to the positive metal ion.

EDTA or ethylenediaminetetraacetate is a **'hexadentate' ligand**; it has 6 negative centres which enable it to form an octahedral complex with a nickel ion trapped in the centre.



One EDTA molecule traps one nickel ion. If the number of moles of EDTA needed to encapsulate all the nickel is found by titration, the number of moles of nickel in the sample can be determined.

Murexide indicator is used because it binds weakly with Ni^{2+} ions and is easily displaced by the EDTA .

The end point can be hard to see . **.88 ammonia solution** is added towards the end point to ensure the EDTA is fully ionised and able to react. This results in a straw coloured solution which turns violet. **NB use the fume cupboard for the .88 ammonia.**

$$\textbf{Ni}^{2+}\textbf{/Indicator} + \textbf{EDTA} \rightarrow [\textbf{EDTA/Ni}^{2+}] + \textbf{indicator}$$

Yellowish Violet

The procedure is carried out in duplicate to establish the reliability/reproducibility of the procedure. If the duplicate results from 2 different samples of the salt give the same or very similar results then the procedure is said to be precise, If many results agree the procedure is reliable. You can share your results with another group to obtain the duplicate results.

Chemicals and Apparatus

- 0.10 mol l^{-1} EDTA solution
- murexide indicator
- Hydrated nickel (II) sulphate ($NiSO_4.6H_2O$)
- 0.88 aqueous ammonia
- 1 mol l^{-1} ammonium chloride
- deionised water
- 100 cm^3 standard flask
- 250 cm^3 conical flasks
- 20 cm^3 pipette
- 50 cm^3 burette
- Weighing bottle
- Balance (accurate to 0.01g)
- 25 cm^3 measuring cylinder
- Pipette filler
- Filter funnel
- White tile
- Wash bottle
- Glass stirring rod
- Dropper

Risk Assessment

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

Hydrated nickel (II) sulphate is harmful by ingestion and inhalation. It irritates the eyes and skin. Continued skin contact can cause dermatitis. Avoid raising a dust. 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 and swallowing causes internal damage. Wear goggles and gloves and handle it in a fume cupboard.

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

Murexide is harmful by ingestion and if inhaled as a dust. It may irritate the eyes.

Nickel(EDTA) complex – limited information is available on its toxicity. Its high stability and water solubility will almost certainly give rise to low toxicity.

Procedure

Part A

Calculate the theoretical percentage by mass of nickel in $NiSO_4.6H_2O$.

Part B

1. Carry out the following procedure **in duplicate**.
2. Weigh accurately by difference approximately 2.6g of hydrated nickel(II) sulphate in a 100 cm^3 beaker.
3. Add about 25 cm^3 of deionised water and stir until fully dissolved.
4. Transfer the solution to a 100 cm^3 standard flask.
5. Rinse the beaker with a little deionised water and add the rinsings to the flask. Repeat this procedure until you are within about a centimetre of the graduation mark on the flask.
6. Using a dropper, make up the solution to the graduation mark with deionised water.
7. Stopper the flask and invert it several times to ensure the contents are thoroughly mixed.
8. Rinse the burette, including the tip, with 0.10 mol l^{-1} EDTA and fill it with the same solution.
9. 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.
10. Add murexide indicator (approximately 0.05g) to the diluted nickel salt solution together with approximately 10 cm^3 of ammonium chloride solution.
11. Titrate the mixture with the EDTA solution and after the addition of about 15 cm^3 of EDTA make the solution alkaline by adding approximately 10 cm^3 of 0.88 aqueous ammonia until the colour is a straw yellow.
12. Continue the titration to the end-point which is shown by the first appearance of a blue-violet colour.
13. Repeat the titrations until two concordant results are obtained.
14. Calculate the moles of EDTA used and thus the moles of Nickel in the aliquot.
15. Multiply this up to find the number of moles in the standard flask and thus the mass of nickel present
16. Calculate the % by mass of nickel in the salt

Calculation Support

The experimental results can be used to calculate the number of moles of nickel in the 100cm^3 solution made up initially since :

1 mol EDTA : 1 mol Ni^{2+}

moles of EDTA used in titration = moles of Ni^{2+} in 20 cm^3 sample

Multiplying by 5 gives the moles of Ni^{2+} in 100cm^3

The mass of nickel present in 100cm^3 can be worked out (m = n x gfm)

The % by mass in the original sample will be

$$\frac{\text{Mass of Nickel}}{\text{Mass of Salt}} \times 100 = \%\text{ by mass}$$

1. Calculate the number of moles of EDTA used. Remember to use the average of the concordant values. Repeat for the duplicate.
2. Calculate the number of moles Ni in each 20 cm^3 aliquot.
3. Calculate the number of moles Ni in the standard flask.
4. Calculate the mass of Ni in the standard flask
5. Calculate the % Ni in the salt (use the mass of Nickel salt you originally added)
6. Work out the % by mass of Ni in the salt, using the GFM from the bottle.
7. Compare your 2 results and comment on their **precision**.
8. Compare your % value with the expected results and comment on the **accuracy** of your results. Accuracy is a measure of how close your practical results are to the theoretical %.
9. Explain why murexide is a suitable indicator to use
10. The main sources of error are the uncertainties in the equipment, the purity of the salt (rarely 100%) and the variable number of moles of water of crystallisation. What are the uncertainties in the equipment?
11. What is the % purity of the salt?
12. What is the no of moles of water of crystallisation given?

Experiment 4   Determination of Chloride

Skills

(a) Weighing by difference and gravimetric analysis
(o) Carrying out stoichiometric calculations

Aim

To determination the number of moles of water in one mole of a sample of barium chloride.

Theory

Gravimetric Analysis

In gravimetric analysis the mass of an element or compound present in a substance is determined by chemically changing that substance into some other substance of known chemical composition, which can be readily isolated, purified and weighed to constant mass.

To determine the number of moles of water of crystallisation in a solid, the weighed substance can be heated strongly and then reweighed. To ensure all the water has been driven off, the substance is heated strongly again and then reweighed. This process is repeated until a constant mass is obtained, when it can be assumed that all the water has been removed. The difference in mass between the initial and final volume enables the mass lost to be determined by difference.

An alternative method converts a soluble substance to a solid precipitate which can be filtered and weighed. The quantity of precipitate allows the quantity of the original substance to be determined. It is essential that the precipitate be allowed to dry completely so the technique of drying and reweighing to constant mass is used. It is important the drying process does not cause the precipitate to decompose.

Determination of hydration

When silver nitrate solution is added to a solution of chloride ions, acidified with nitric acid, insoluble silver (I) chloride precipitates and can be collected by filtration.

$$Cl^-(aq) + \quad Ag^+ \quad (aq) \quad \rightarrow \quad AgCl\ (s)$$

The experiment is best carried out in subdued light since the precipitate is photosensitive, decomposing into silver and chlorine.

The chemical formula of Hydrated Barium Chloride is:

$$BaCl_2.xH_2O$$

To calculate x (the number of moles of water), we can first calculate the mass and number of moles of Baroium chloride in each sample. The remainder of the sample will be water and thus x can be determined by mole ratio.

Chemicals and Apparatus

- Hydrated barium chloride
- Silver(l) nitrate solution (0.5 mol l-1)
- Very dilute nitric acid (about 0.01 mol l-1)
- Sintered-glass crucible (porosity 3)
- Buchner flask and adapter
- Stirring rod with rubber ‘policeman’
- Concentrated nitric acid
- Beaker (400 cm^3)
- Wash bottle
- Filter pump

Risk Assessment

Barium chloride is harmful by inhalation and by ingestion or skin contact. It is a possible mutagen or teratogen. Wear eye protection and gloves. Wash any spillages off the skin with water.

Nitric acid, concentrated – causes severe burns to skin and eyes; vapour is irritant and harmful. Wear eye protection and PVC gloves.

Silver nitrate is harmful by ingestion (LD50 0.05g/kg) and causes severe burns to eyes and skin. Wear eye protection and gloves.

Silver(I) chloride (product) is harmful by skin contact, inhalation and by ingestion; is irritating to the eyes and skin.

Dispose of both silver compounds into silver residue bottle.

Procedure

1. Weigh accurately by difference AR approximately 0.8 – 1.0 g hydrated barium chloride into a 400 cm^3 beaker.
2. Dissolve the chloride in distilled water (about 100 cm^3) and acidify the solution with about 1 cm^3 of concentrated nitric acid.
3. Add slowly, with stirring 0.5 mol l^{-1} silver(I) nitrate (20 cm^3). This should be an excess.
4. Stir the mixture by rubbing the ‘policeman’ on the inside of the beaker to encourage the precipitate to coagulate.
5. When clear, test the supernatant liquid with one drop of silver(I) nitrate solution to see whether precipitation is complete.
6. Dry the sintered-glass crucible in a desiccator and weigh. Repeat until no further loss of mass is seen.
7. Set up the filtration apparatus and carefully transfer the precipitate to the sintered-glass crucible with washings.

8. Wash the precipitate with two or three 10 cm^3 portions of very dilute nitric acid to remove traces of soluble salts and pour the filtrate into the “silver residues” bottle.
9. Wash out the Buchner flask, reassemble the filtration apparatus and add a further portion of 0.01 $moll^{-1}$ nitric acid. Test the filtrate with dilute hydrochloric acid. If no precipitate appears, all traces of silver ions have been removed.
10. Place the crucible in a clean beaker, cover with a watch glass and dry
11. Weigh the crucible and precipitate.
12. Repeat the drying to constant mass.
13. Calculate the mass of chloride ions in the sample.
14. Use this to calculate the mass and number of moles of Barium Chloride in the original sample.
15. Use this to calculate the mass and number of moles of water in the original sample.
16. Use the ratio of moles $BaCl_2$:moles H_2O to determine x in $BaCl_2xH_2O$

Experiment 5 Preparation of Potassium Trioxalatoferrate(III)

Skills

(i) Using vacuum filtration methods
(j) Recrystallising
(k) Determining % yield experimentally
(o) Carrying out stoichiometric calculations

Aim

To prepare a sample of Potassium Trioxalatoferrate(III) and calculate the percentage yield

Theory

Recrystalisation

Recrystallisation is a laboratory technique used to purify solids, based upon solubility. The solvent for recrystallisation must be carefully selected such that the impure compound is insoluble at lower temperatures, yet completely soluble at higher temperatures. The impure compound is dissolved gently in the minimum volume of hot solvent then filtered to remove insoluble impurities. The filtrate is allowed to cool slowly to force crystallisation. The more soluble impurities are left behind in the solvent. The pure crystals may be separated from the filtrate using vacuum filtration or filtration under pressure.

Vacuum Filtration

These methods are carried out under reduced pressure and provide a faster means of separating the precipitate from the filtrate. The choice of filtering medium depends on the quantity and nature of the precipitate.

Determination of percentage yield

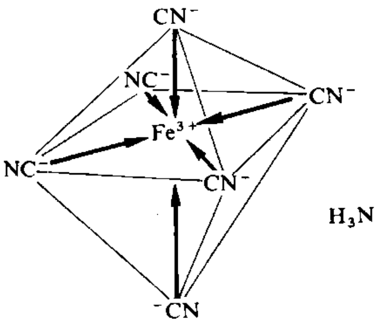
Percentage yields can be calculated from the number of moles of limiting reagent used and the number of moles of product formed. Mass transfer or mechanical losses and purification of product inevitably lowers the percentage yield.

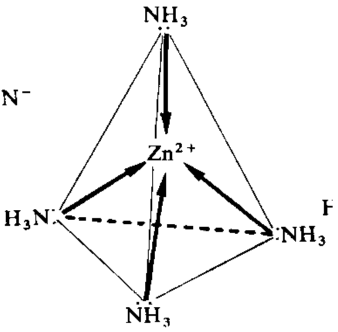
Preparation of Potassium Trioxalatoferrate(lii)

The preparation of Potassium Trioxalatoferrate) brings together all 3 of the above techniques.

Please note the safety information from SSERC re bumping

Potassium trioxalatoferrate(lll) K_3^{+} $[Fe(C_2O_4)_3]^{3-}$ contains the negatively charged complex ion, trioxalatoferrate (lll).





The name of the ion shows that it contains an Fe^{3+} ion (shown by the roman numerals) surrounded by three (tri) oxalate ions.

Transition metals often form complex ions in which a positive metals ion is surrounded by **ligands.**

Ligands are either negative ions or molecules that have unbonded electrons which act as negative 'centres'.

One theory suggests that the negative centres or the negatively charged ions are attracted to the central positive transition metal ion. Oxalate ions are able to act as ligands because they are negative ions.

Complex ions commonly have 4 ligands in a tetrahedral or 6 ligands in an octahedral arrangement

The three oxalate ions in the trioxalatoferrate ion give an **octahedral arrangement**.

There is an overall negative 3 charge because the three oxalate ions have a 2 negative charge:

$$Fe(3+) + \quad 3 \times C_2O_4(2-) \quad = \quad 3-$$

Chemicals and Apparatus:

- hydrated ammonium iron(II) sulphate
- 20 volume’ hydrogen peroxide
- deionised water
- potassium oxalate solution
- dilute sulphuric acid
- oxalic acid solution
- ethanol
- hot plate
- glass stirring rod
- 100 cm^3 glass beakers
- 25 cm^3 measuring cylinder
- balance (accurate to 0.01g)
- thermometer
- dropper
- glass filter funnel
- filter papers
- 100 cm^3 crystallising basin
- clock glass

Risk Assessment

Wear eye protection and if any chemical splashes on your skin wash it off immediately.
Hydrated ammonium iron(II) sulphate may be harmful if ingested and may irritate the eyes. Wear gloves.
Oxalic acid solution, potassium oxalate solution and the product, **potassium trioxalatoferrate(III),** are all harmful by ingestion and are irritating to the eyes and skin. Wear gloves.
‘20 volume’ hydrogen peroxide is irritating to the eyes and skin. Wear gloves.
Ethanol is volatile, highly flammable, irritating to the eyes and intoxicating if inhaled or ingested.
Dilute sulphuric acid is corrosive. Wear gloves.
READ THE SAFETY INFORMATION ON THE ‘BUMPING’ PROBLEM THAT CAN HAPPEN DURING THIS PREPARATION BEFORE CONTINUING (page 24)

Procedure

1. Weigh a $100cm^3$ glass beaker and to it, add approximately 5g of hydrated ammonium iron(II) sulphate, $(NH_4)_2Fe(SO_4)_2.6H_2O$. Reweigh the beaker and its contents.

2. Add approximately 15 cm^3 of deionised water and 1 cm^3 of dilute sulphuric acid to the ammonium iron(III) sulphate.
3. Once the ammonium iron(III) sulphate has dissolved, add 25 cm^3 of oxalic acid solution.
4. Place the beaker on a hot plate/stirrer and slowly heat the mixture with stirring until it boils.
5. Remove the beaker from the heat and allow the precipitate of iron(II) oxalate to settle to the bottom of the beaker.
6. Decant off the liquid and add about 50 cm^3 of hot deionised water to the precipitate. Stir the mixture and after the precipitate has settled once more, decant off the liquid.
7. Add 10 cm^3 of potassium oxalate solution to the washed precipitate and heat the mixture to about 40°C.
8. To this mixture, add **slowly** with continuous stirring, 20 cm^3 of '20 volume' hydrogen peroxide solution. Keep the temperature close to 40°C during the addition of the hydrogen peroxide.All the yellow precipitate should be converted to a brown precipitate.
9. Heat the mixture nearly to boiling and add oxalic acid solution, dropwise with stirring, until the brown precipitate of iron(III) hydroxide dissolves and a clear green solution is obtained. Take care not to add too much oxalic acid. During the addition of the oxalic acid, keep the reaction mixture near to boiling.
10. Filter off the hot solution through fluted filter paper into a crystallising basin – this is to remove impurities. No crystals should be seen in the filter paper or funnel.
11. Add 25 cm^3 ethanol to the filtrate and if any crystals form, re-dissolve them by gentle heating.
12. Cover the solution with a filter paper and set aside in a dark cupboard for crystallisation to take place.
13. Filter off the crystals and wash them with a 1:1 mixture of ethanol and water.
14. Weigh a clock glass and transfer the crystals to it. Cover the crystals with a filter paper and leave them to dry at room temperature in a dark cupboard.
15. Once dry, reweigh the crystals and clock glass.
16. Calculate the percentage yield of hydrated potassium trioxalatoferrate(III), $K_3([Fe(C_2O_4)_3].3H_2O$.

Calculation & Write Up Support

Write the 3 equations in your lab book and answer the questions

Steps 1- 5

Ammonium iron (ll) sulphate is reacted with oxalic acid. A precipitate of iron(ll)oxalate is formed. The other product is ammonium hydrogen sulphate.

$$(NH_4)_2 Fe (SO_4)_2 + (COOH)_2 \rightarrow Fe (COO)_2 + 2NH_4 HSO_4$$

1. Note the colour of the precipitate formed.

Steps 6-8

The washed iron (ll) oxalate precipitate reacts with hydrogen peroxide and potassium oxalate to give potassium trioxalatoferrate and iron (lll)hydroxide.

$$3Fe(COO)_2 + \frac{3}{2}H_2O_2 + 3K_2(COO)_2 \rightarrow Fe(OH)_3 + 2K_3[Fe(C_2O_4)_3]$$

1. Note the colour of the iron hydroxide precipitate formed.
2. Look up the ion electron half equation for the change in the Fe ion.
3. What was the purpose of the hydrogen peroxide?

Step 9:

Iron hydroxide is reacted to yield more potassium trioxalatoferrate. The equation for this reaction is

$$2Fe(OH)_3 + 3K_2(COO)_2 + 3(COOH)_2 \rightarrow 2K_3[Fe(C_2O_4)_3] + 6H_2O$$

1. Note the colour of potassium trioxalatoferrate.
2. Calculate the expected mass of product. Overall, there is a 1mol:1mol ratio. Don't forget to include the water of crystallisation in the gfm.
3. Calculate the yield
4. Evaluation: Explain why the yield is less than 100%. Note the sources of error in the procedure and in the results.
5. Explain what is meant by recrystallisation and why vacuum filtration is used.
6. Explain how the oxalate ion is able to act as a ligand
7. Draw the shape of the trioxalatoferrate ion and give the name of this shape.

Bumping during the preparation of potassium trioxalatoferrate(III)

Some improvements are recommended to the method of preparing potassium trioxalatoferrate(III) (Advanced Higher Chemistry PPA, Unit 1, PPA 1)

"Then nightly sings the staring owl:

'Tu-who;

Tu-whit, Tu-who' - A merry note,

While greasy Joan doth keel the pot"

LOVE'S LABOURS LOST Shakespeare

We recently received a report of a problem regarding this PPA. This incident occurred during Step 4 of the Procedure, when bringing the aqueous solution and the yellow precipitate of iron(II) oxalate (ethanedioate) to the boil on a hotplate. It was reported that the solution sometimes erupted violently and ejected the contents some distance, and that this happened before reaching the boiling point. We have taken the opportunity here to highlight a second potential problem which can arise during the addition of hydrogen peroxide solution in Step 8.

We repeated the preparation several times and confirmed that the problem exists, but that it can be overcome. Hotplates are often difficult to control; they are fine for hard boiling and refluxing or for slow simmering, but unless you know the peculiarities of the particular hotplate, can be difficult to control at in-between rates of heating. The delay in response to any change of the heat setting, whether an increase or decrease, often catches out the uninitiated or the impatient. The surface temperature of a hotplate on a high setting is typically in excess of 300 °C and even water, if small in volume, will bump on this. It is useful to roughly calibrate your hotplates by trial and error and mark the setting at which water just boils gently.

The following points relating to the procedure were identified:

Step 4 - When the beaker is placed on the hotplate adjusted to a low rate of heating as per instructions (setting 3 on our hotplate), then this Step can take a long time, - too long. It is possible to heat the solution faster (setting 5 on our hotplate), but then stirring **must** be continuous to prevent the solution from splattering, the best method being to use a magnetic stirrer hotplate. Hand stirring with a glass rod will do the job, but must be continuous.

Step 6 - Once you have decanted off the hot water, let the solution cool slightly before continuing. We found the temperature of the beaker at this point to be well above 40 °C.

Step 7- Addition of the 10 cm^3 of potassium oxalate (ethanedioate) solution cooled the beaker contents to a temperature of 35 °C. The solution was heated until it reached 40 °C and then removed from the hotplate.

Step 8 – The initial addition of the 20 volume hydrogen peroxide needs to be in amounts of less than 1 cm^3 as the oxidation is highly exothermic and the temperature of the beaker contents can rise well above 40 °C. The reaction is very vigorous and the liquid can froth over. We would recommend cooling the beaker in a cold water bath during the hydrogen peroxide additions until more than half of the hydrogen peroxide (approximately 13 cm^3) had been added. Thereafter the addition can probably be made more rapidly.

So the general advice on good practice in preparations is:

(i) to stir well and

(ii) when adding reagents, to initially make small additions with efficient mixing and check that the reaction is occurring and that most of the portion just added has been used up before making the next addition.

"Make the gruel thick and slab;

Add thereto a tiger's cauldron,

For th'ingredience of our cauldron.

Double, double toil and trouble;

Fire burn, and cauldron bubble."

MACBETH Shakespeare

New chemical nomenclature!

Recently spotted on the wrapper of a bar of soap are two names based on yet another system;

"Sodium tallowate and sodium cocoate".

Here sodium cocoate (presumably either sodium dodecanoate or hexadecanoate or perhaps a mixture of the two) combines the new and the old; the IUPAC ending of "oate" has been grafted onto the cocoa palm tree, indicating the natural source of the substance. Would sodium rhubarbanoate or sodium sorrelanoate be alternatives to sodium ethanedioate or would sodium willowate tell us more about its origins than sodium 2-hydroxybenzenecarboxylic acid?

Experiment 6 Preparation and Analysis of Aspirin

Skills

(j) Recrystallising
(k) Determining % yield experimentally
(l) Using thin-layer chromatography
(m) Using melting point apparatus and mixed melting point determination
(o) Carrying out stoichiometric calculations

Aim

To prepare and determine the purity of a sample of Aspirin

Theory

Melting Point

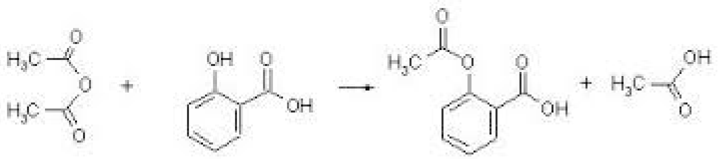
The melting point of an organic compound is one of several physical properties by which it can be identified. A crystalline substance has a sharp melting point falling within a very small temperature range. Determination of the melting point can also give an indication of the purity of an organic compound, as the presence of impurities lowers the melting point and extends its melting temperature range.

Since impurities lower the melting point, the technique of mixed melting point determination can be used as a means of identifying the product of a reaction

Preparation of Aspirin

Aspirin is an ester of 2-hydroxybenzoic acid (salicylic acid) and ethanoic acid. However, the reactants you will use are 2-hydroxybenzoic acid and ethanoic anhydride, which is formed by the condensation of 2 molecules of ethanoic acid.

Step 1 :



In step 2 the ethanoic acid formed reacts with the 2-hydroxybenzoic acid to produce aspirin and water.

This reaction is less violent and also enables a greater yield to be achieved as the equilibrium is pushed further to the right. This is because the anhydride only produces 0.5 mole of water per mole of alcohol, whereas using ethanoic acid would produce 1 mol of water. The catalyst removes water from the RHS of the equilibrium, and this is easier if less water is formed.

The aspirin formed can be purified by recrystallisation and the melting point determined to assess the purity of the sample

thin-layer chromatography

Instead of chromatography paper, thin-layer chromatography (TLC) uses a fine film of silica or aluminium oxide spread over glass or plastic. Separation is usually faster and better than with paper chromatography.

R_f values can be calculated and under similar conditions a compound will always have the same Rf value within al error.

Since a pure substance will show up as only one spot on the developed chromatogram, TLC can be used to assess the purity of a product prepared in the lab.

In this experiment recrystallised samples of aspirin are compared with a known sample of aspirin.

Chemicals and Apparatus:

- 2-hydroxybenzoic acid
- ethanoic anhydride
- ice
- 100 cm^3 conical flasks
- 85% phosphoric acid
- Ethanol
- anti-bumping granules
- deionised water
- Ethanol
- aspirin
- Dichloromethane
- Iodine resublimed
- measuring cylinders (10 cm^3 , 50 cm^3)
- 250 cm^3 glass beakers
- Thermometers
- dropper
- balance (accurate to 0.01g)
- hot plate
- 50 cm^3 conical flask
- filter papers

- clock glass
- melting point apparatus
- capillary tube
- TlC plates

Risk Assessment

Wear eye protection and if any chemical splashes on your 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.
80% 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.
Ethanol is volatile, highly flammable, irritating to the eyes and intoxicating if inhaled or ingested.

Procedure 1 – Preparation of Aspirin

1. Weigh a 50cm^3 conical flask and to it, add about 5g of 2-hydroxybenzoic acid. Reweigh the flask and its contents
2. In a fume cupboard, add 10cm^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 5 drops of 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. Hold 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 150cm^3 of cold water contained in a 250cm^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 15cm^3 of ethanol in a 100cm^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 100cm^3 conical flask containing about 40cm^3 of water. If an oil forms, re-heat the mixture on the hot plate to dissolve it. If the oil still persists, add a few drops of ethanol and re-heat 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.

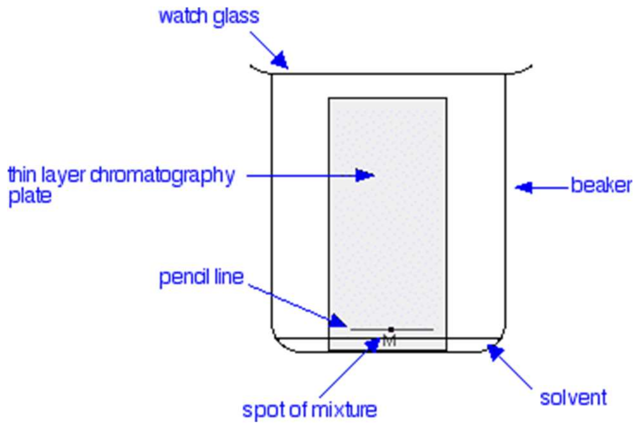
12. Determine the melting point of the aspirin.
13. Calculate the percentage yield of aspirin.
14. Keep the aspirin for a later experiment.

Calculation & Write Up Support

1. Using structural formulae write the overall equation for the condensation reaction between 2-hydroxybenzoic acid and ethanoic anhydride.
2. Why would the equilibrium move further to the right than if ethanoic acid was used?
3. Calculate the expected mass of aspirin and thus the yield.
4. The accepted melting point of aspirin is 137°C. Comment on the purity of your sample.

Procedure 2 – Thin Layer Chromatography of Aspirin

1. Make sure that you do not touch the surface of the tlc plate with your fingers during this activity. Handle the plate only by the edges and use tweezers if possible.
2. Take a tlc plate and using a pencil (not a biro or felt tip pen) lightly draw a line across the plate about 1 cm from the bottom. Mark three equally spaced points on this line.
3. Place small amounts (about 1/3 of a spatula measure) of your recrystallised aspirin and the commercial sample of aspirin in two separate test tubes. Label the test-tubes so that you know which is which.
4. Make up 5 cm^3 of solvent by mixing equal volumes of ethanol and dichloromethane in a test-tube. Add 1 cm^3 of the solvent to each of the test-tubes to dissolve the samples. If possible do this in a fume cupboard.
5. Use capillary tubes to spot each of your samples onto the tlc plate. Allow the spots to dry and then repeat three more times. The spots should be about 1–2 mm in diameter.
6. After all the spots are dry, place the tlc plate in the developing tank making sure that the original pencil line is above the level of the developing solvent – ethyl ethanoate. Put a lid on the tank and allow to stand in a fume cupboard until the solvent front has risen to within a few millimetres of the top of the plate.



7. Remove the plate from the tank and quickly mark the position of the solvent front. Allow the plate to dry.
8. Observe the plate under a short wavelength UV lamp and lightly mark with a pencil any spots observed.
9. Carefully place the plate in a jar or beaker containing a few iodine crystals. Put a cover on the jar and warm gently on a steam bath until spots begin to appear. Do this in a fume cupboard if possible.

Experiment 7 Preparation of Benzoic Acid

Skills

(c) Using a reference or control or blank determination
(h) Refluxing
(i) Using vacuum filtration methods
(j) Recrystallising
(k) Determining % yield experimentally
(m) Using melting point apparatus and mixed melting point determination
(o) Carrying out stoichiometric calculations

Aim

To prepare a pure sample of benzoic acid by hydrolysis of ethyl benzoate

Theory

Refluxing

Refluxing is a technique used to apply heat energy to a chemical reaction mixture over an extended period of time. The liquid reaction mixture is placed in a round-bottomed flask with a condenser connected at the top. The flask is heated vigorously over the course of the chemical reaction; any vapours given off are immediately returned to the reaction vessel as liquids when they reach the condenser.

This technique provides opportunities for you to become familiar with glassware containing ground glass joints.

Quick fit apparatus sets are designed to fit perfectly together. It is often advisable to apply a small amount of Vaseline to the joints so that the glassware can easily be separated.

Use of a control or reference

A control determination consists of carrying out a determination on a solution of known concentration to establish the validity of the results. A control can also be used for analysis of solids such as when determining melting points. For example, to check the purity of a prepared sample of aspirin, a melting point would be determined and this can be compared to the melting point of pure salicylic acid.

A blank determination consists of carrying out a separate determination without the substance being tested for being present.

Determination of melting point and mixed melting point

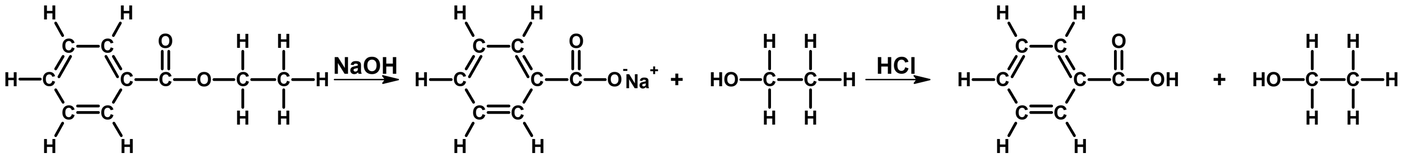
The melting point of an organic compound is one of several physical properties by which it can be identified. A crystalline substance has a sharp melting point falling within a very small temperature range. Determination of the melting point can also give an indication of the purity of an organic compound, as the presence of impurities lowers the melting point and extends its melting temperature range.

Since impurities lower the melting point, the technique of mixed melting point determination can be used as a means of identifying the product of a reaction

Preparation of Benzoic Acid by Hydrolysis Of Ethyl Benzoate

Treatment of an ester with aqueous base results in the hydrolysis of the ester with the formation of the salt of the acid and an alcohol.

For example, hydrolysis of ethyl benzoate yields sodium benzoate and ethyl alcohol.



Hydrolysis = splitting by water. The usual catalyst is sodium hydroxide. Heating under reflux allows you to heat the reaction mixture for an extended period without loss of volatile compounds.

ESTER + WATER ⇌ ACID + ALCOHOL

The catalyst neutralises the acid formed in the hydrolysis, moving the equilibrium to the right. At the end of the hydrolysis you will have the remaining ester, the unreacted catalyst, the sodium salt of benzoic acid and ethanol in the flask!

The solid benzoic acid can be displaced from the solution by adding a stronger acid. The solid acid can then be purified by recrystallisation and the melting point determined to assess the purity of the sample.

Chemicals and Apparatus:

- ethyl benzoate
- 2 mol l^{-1} sodium hydroxide
- 5 mol l^{-1} hydrochloric acid
- anti-bumping granules
- Buchner funnel and flask
- blue litmus paper or pH paper
- 100 cm^3 round-bottomed flask
- 100 cm^3 measuring cylinder
- deionised water
- heating mantle
- Condenser
- glass filter funnel
- melting point apparatus
- cork ring
- capillary tube
- thermometer
- water pump
- balance (accurate to 0.01g)
- oven
- hot plate
- filter papers
- 250 cm^3 glass beakers
- clock glass
- glass stirring rod
- dropper

Risk Assessment

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

Ethyl benzoate is off low volatility and flammability. It irritates the eyes and is harmful if ingested in quantity.

2 mol l^{-1} **sodium hydroxide** is corrosive to the eyes and skin. Gloves and goggles should be worn.

5 mol l^{-1} **hydrochloric acid** is irritating to the eyes, lungs and skin and if swallowed. Wear gloves.

The product, **benzoic acid** is of low volatility and flammability. It may be harmful if ingested in quantitiy.

Only a small amount of **ethanol** is produced in the reaction. It is volatile, highly flammable, irritating to the eyes and intoxicating if inhaled or ingested.

Procedure:

1. Weigh the 100 cm^3 round-bottomed flask supported on a cork ring. To the flask, add about 5g of ethyl benzoate and reweigh the flask and its contents.
2. To the ethyl benzoate, add approximately 50 cm^3 of 2 mol l^{-1} sodium hydroxide and a few anti-bumping granules.
3. Set up the apparatus for heating under reflux. Using a heating mantle, reflux the reaction mixture until all oily drops of the ester have disappeared. This may take 45 – 60 minutes.
4. Allow the apparatus to cool and then transfer the reaction mixture to a 250 cm^3 beaker.
5. Slowly and with stirring, add 5 mol l^{-1} hydrochloric acid to the reaction mixture to precipitate out the benzoic acid. Continue adding the acid until no more precipitation takes place and the mixture turns acidic – test with blue litmus paper or pH paper. (About 30 cm^3 of acid will be required).
6. Allow the mixture to cool to room temperature and filter off the precipitate at the water pump and wash the crude benzoic acid with a small volume of water.
7. Transfer the crude benzoic acid to a 250 cm^3 beaker and recrystallise it from about 100 cm^3 of water.
8. Filter off the crystals of benzoic acid at the water pump and wash them with a small volume of water. Allow air to be drawn through the crystals for a few minutes in order to partially dry them.
9. Weigh a clock glass and transfer the crystals to it. Dry the crystals in an oven at about 70°C and then reweigh the clock glass and crystals.
10. Determine the melting point of the benzoic acid you made and of a sample of commercial benzoic acid.
11. Calculate the percentage yield of benzoic acid.

Calculation & Write Up Support

1. Using structural formulae write the equation for the reaction
2. Using structural formulae write the equation for the displacement of the benzoic acid from the sodium benzoate
3. Work out the expected mass of benzoic acid and thus the percentage yield.
4. The accepted value of the melting point of benzoic acid is 121°C.
5. Comment on the purity of your sample
6. Explain why the yield was less than 100%.
7. What would be the effect on the yield if HCl was used as the catalyst instead of NaOH?

Experiment 8 Determination of Manganese in Steel

Skills

(c) Using a reference or control or blank determination

(f) Using a colorimeter or visible spectrophotometer and carrying out dilution to prepare a calibration graph

(o) Carrying out stoichiometric calculations

Aim

To determine the % of manganese in a paper clip

Theory

Colorimetric determination of manganese in steel uses potassium permanganate of known concentration to produce a series of dilutions whose absorbance is measured and used to produce a calibration graph. The manganese in steel is then oxidised to permanganate, and the concentration of the resulting solution is found from the graph.

Colorimetry is a useful technique to determine the concentration of coloured ions. It is particularly suitable to the determination of manganese in steel because manganese can be oxidised to the coloured permanganate ion. The absorbance of the solution formed can be compared to a calibration graph, and this will enable the concentration of the solution to be determined.

The colorimeter compares the intensity of the incident light with the intensity of the transmitted light according to **Beers's Law**.

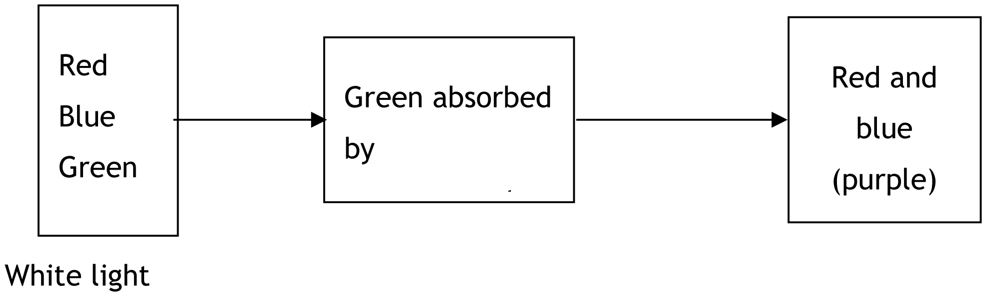
$$\textbf{Asorbance } A = \frac{\log I_o}{\log I}$$

I_o is the intensity of the incident light

I is the intensity of the transmitted light

The more concentrated the compound, the less light will be transmitted. The colour of incident light is controlled by the filter.

Compounds appear coloured because they absorb certain wavelengths of light. The permanganate ion appears purple because it absorbs green light, leaving red and blue to be transmitted to the eye.



A green filter is used because purple permanganate ions absorb green light and so green will give the highest absorbance reading at low concentrations.

The higher the concentration of permanganate ions, the more green light is absorbed.

In part A of the procedure, a series of solutions of known concentration are made up and their absorbance recorded. The data obtained can be used to draw a calibration graph.

The solutions are prepared by dilution from a standard solution. The concentration of each of the $50cm^3$ standard flasks can be calculated using the relationship:

$$C_1V_1 = C_2V_2$$

The absorbance of an unknown can now be measured and the graph used to find it's concentration.

In part B of the procedure, manganese atoms in steel are oxidised in two stages to permanganate ions. The pupil instruction sheet shows clearly the two stages involved.

Eventually all the manganese atoms in the steel will have been converted into permanganate ions. The ions will be transferred to a standard flask which is made up to $100\ cm^3$. The concentration of the permanganate ions can be determined by colorimetry. This gives the number of moles in $1000cm^3$.

The number of moles in $100cm^3$ can be deduced and this will be equal to the number of moles of manganese atoms in the steel.

$$Mn \rightarrow Mn^{2+} \rightarrow MnO_4$$

The mass of manganese in the steel can be calculated and used to find the % by mass in the paper clip.

The procedure is carried out in duplicate.

This uses potassium permanganate of known concentration to produce a series of dilutions whose absorbance is measured and used to produce a calibration graph. The manganese in steel is then oxidised to permanganate, and the concentration of the resulting solution is found from the graph.

Chemicals and Apparatus

- Steel paper clips
- 0.0010 mol l^{-1} acidified potassium permanganate
- 2 mol l^{-1} nitric acid
- 85% phosphoric acid
- propanone
- deionised water
- 50 cm^3 burette
- Colorimeter
- 540 nm filter
- optically matched cuvettes acidified potassium periodate solution
- balance (accurate to 0.001g) potassium persulphate
- glass beakers (50 cm^3 and 250 cm^3)
- 100 cm^3 and 100 cm^3 standard flasks
- Bunsen burner, heating mat and tripod
- Measuring cylinders (50 cm^3 and 10 cm^3)
- anti-bumping granules
- Clock glass
- Filter funnel
- Tweezers
- Wash bottle
- Dropper
- Wire cutters

Risk Assessment

Wear eye protection and if any chemical splashes on your skin wash it off immediately.
The acidified 0.0010 mol l-1 potassium permanganate is harmful in ingested and irritates the eyes and skin. Wear gloves.
Both 2 mol l-1 nitric acid and its vapour are corrosive and toxic causing severe burns to the eyes, digestive and respiratory systems and in contact with the skin. Wear gloves.
85% phosphoric acid is corrosive; it burns and irritates the eyes and skin. 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 persulphate 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.

Procedure: Part A – Calibration graph

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. Use a dropper for the final centimetre.
3. Stopper the flask and invert it several times to ensure the contents are completely mixed.
4. Rinse a cuvette with some of this solution and fill it.
5. Using the colorimeter (fitted with a 520nm filter) measure the absorbance of the solution in the cuvette.
6. Repeat steps two to five with 4, 6, 8, 10, 12 and 14 cm^3 of the permanganate stock solution in the burette.
7. Plot a calibration graph of 'absorbance' against 'concentration of potassium permanganate'. Your teacher will provide you with the accurate concentration of the potassium permanganate stock solution.

Procedure: Part B – Conversion of manganese to permanganate

1. Carry out the following procedure in **duplicate.**
2. Degrease a steel paper clip by swirling it with a little propanone in a small beaker. Using tweezers, remove the paper clip and leave it to dry for about a minute or so on a paper towel.
3. Cut up the paper clip into small pieces.
4. Weigh accurately about 0.2g of the paper clip pieces and transfer them to a 250 cm^3 glass beaker.
5. Add approximately 40 cm^3 of 2 mol l^{-1} nitric acid to the beaker and cover it with a clock glass.
6. Heat the mixture cautiously, in a fume cupboard, until the reaction begins. Continue hearting gently to maintain the reaction, but remove the source of heat if it becomes too vigorous.
7. Once the steel has dissolved, 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.
8. After the solution has cooled considerably – no more than 'hand hot' – add about 5 cm^3 of 85% phosphoric acid, approximately 0.2g of potassium persulphate and a couple of fresh anti-bumping granules. Boil the mixture for about 5 minutes.
9. 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 should start to turn pink. Continue gentle boiling until the intensity of the pink colour remains constant. This should take about 5 minutes.
10. 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.

11. Rinse the beaker with a little deionised water and add the rinsings (but not the anti-bumping granules) to the flask. Repeat this procedure until you are within about a centimetre of the graduation mark on the flask.
12. Using a dropper, make up the solution to the graduation mark with deionised water.
13. Stopper the flask and invert it several times to ensure the contents are completely mixed.
14. Using a colorimeter fitted with a 540nm filter, measure the absorbance of the solution.
15. 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.

Calculation & Write Up Support

1. From your graph, deduce the concentrations of permanganate in your 2 samples.
2. Calculate the number of moles of permanganate in the standard flask and thus the moles of manganese in the paper clip.
3. Calculate the mass of manganese in each paper clip using m= n x gfm
4. Calculate the % of manganese in each paper clip.

$$\frac{\text{Mass of Manganese}}{\text{Mass of Paper clip}} \times 100 = \%\text{ by mass}$$

5. Precise – the duplicate results are in close agreement with each other
6. Accurate – the duplicate results are in close agreement with the known true value.
7. Compare the two results you have obtained and comment on how precise they are.
8. Why can you not comment on how accurate they are?
9. Fully explain why colorimetry is a suitable method for determining manganese in steel. Draw a diagram of the way light passes through the filter and the sample and explain what is meant by absorbance.
10. Why is a green filter used?
11. Why are optically matched cuvettes used?

Experiment 9 Preparation of Cyclohexene

Skills

(g) Distilling
(k) Determining % yield experimentally
(n) Using a separating funnel and solvent extraction
(o) Carrying out stoichiometric calculations

Aim

To prepare a sample of cyclohexene from cyclohexane and determine the percentage yield

Theory

Distillation

Distillation is the process of heating a liquid until it boils, capturing and cooling the resultant hot vapours, and collecting the condensed vapours. In the modern organic chemistry laboratory, distillation is a powerful tool, both for the identification and the purification of organic compounds. The boiling point of a compound—determined by distillation—is well-defined and thus is one of the physical properties of a compound by which it is identified.

Distillation is used to purify a compound by separating it from a non-volatile or less-volatile material. When different compounds in a mixture have different boiling points, they separate into individual components when the mixture is carefully distilled.

Steam distillation may be used where the compound might decompose on heating. Steam distillation increases the pressure within the distillation vessel, lowering the boiling points. In addition, the presence of water/steam and the compound as a mixture, will lower the boiling point.

Solvent extraction/ Use of a separating funnel

Solvent extraction is an application of the partition of a solute between two liquids. It is based on the relative solubility of a compound in two different immiscible liquids, usually water and an organic solvent.

The two solvents form two separate layers in the separating funnel and the lower layer is run off into one container and the upper layer is poured out into another container. The quantity of solute extracted depends on the partition coefficient and on the number of times that the process is repeated.

A suitable solvent must be used. For example, supercritical CO_2 is used in the preparation of decaffeinated coffee commercially.

Preparation of Cyclohexene By Dehydration Of Cyclohexanol

In this experiment, cyclohexene is prepared by a dehydration reaction. The cyclohexene is collected **by distillation** and purified using a **separating funnel**.
The products are shaken with sodium chloride solution in order to dissolve the excess reactants and then dried with anhydrous calcium chloride. Na Cl solution is used instead of pure water as it has a higher density and will settle out from the organic product more rapidly.

Chemicals and Apparatus:

- cyclohexanol
- 85% phosphoric acid
- saturated sodium chloride solution
- anhydrous sodium chloride solution
- anti-bumping granules
- cork ring
- Condenser
- still head
- receiver adapter
- thermometer adapterbromine solution
- thermometer
- balance (accurate to 0.01g)
- 50 cm^3 round-bottomed flasks
- heating mantle
- 250 cm^3 separating funnel
- clamp stands and clamps
- 10 cm^3 measuring cylinder
- 50 cm^3 conical flask
- test tube and rack
- dropper

Risk Assessment

Wear eye protection and if any chemical splashes on your skin wash it off immediately.
Cyclohexanol and its vapour are harmful to the eyes, lungs and skin and if swallowed. It irritates and is absorbed through the skin. It is flammable and is a suspected carcinogen. Wear gloves.
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.
Anhydrous calcium chloride irritates the eyes, lungs and skin. Wear gloves.

Cyclohexene is highly flammable and its vapour is moderately toxic to the eyes, skin and respiratory system. It is harmful if swallowed. Wear gloves. At the end of the experiment, dispose of the cyclohexene since it may form unstable peroxides if it is stored.

Bromine solution causes burns and is toxic. Wear gloves. If any splashes on the skin, wash it off with sodium thiosulphate solution.

Procedure

1. Weigh a 50cm^3 round-bottomed flask supported on a cork ring. To the flask, add about 20g of cyclohexanol and reweigh the flask and its contents.
2. To the cyclohexanol, add dropwise with swirling approximately 8 cm^3 85% phosphoric acid.
3. Add a few anti-bumping granules to the reaction mixture and set up the apparatus for distillation. **Gently** heat the mixture for about 15 minutes – do not allow it to boil. Raise the temperature and distil the mixture very **slowly**, collecting the liquid which comes over between 70 and 90°C.
4. Wash the distillation apparatus and leave it to dry.
5. Pour the distillate into a separating funnel and add about an equal volume of saturated sodium chloride solution. Stopper the funnel and shake the contents vigorously. (Sodium chloride solution is used rather than water because it is more dense and will separate from the cyclohexene more rapidly)
6. Clamp the separating funnel and allow the two layers to separate.
7. Remove the stopper from the funnel and run off the lower aqueous layer into a beaker and dispose of it down the sink.
8. Run the top layer (the crude alkene) into a small conical flask and add a few pieces of anhydrous calcium chloride. Stopper the flask and shake the mixture for a few minutes until the liquid is clear.
9. Weigh a dry 50cm^3 round-bottomed flask in which to collect the pure cyclohexene.
10. Decant the alkene into another dry 50cm^3 round-bottomed flask and add a few anti-bumping granules. Distil the alkene very slowly collecting the liquid which comes over between 81 and 85°C in the pre-weighed flask.
11. Weigh the flask and product.
12. Carry out a test to show that the product is unsaturated.
13. Calculate the percentage yield of cyclohexene

Calculation & Write Up Support

1. Write the equation for the dehydration of cyclohexanol and calculate the mass of cyclohexene you expect to obtain.
2. Draw a labelled diagram for the distillation process
3. Calculate your % yield
4. Why is the yield less than 100%?
5. Why is phosphoric acid used instead of sulfuric acid?