Determining the concentration of copper(II) ions Using various analytical techniques

There are various analytical techniques that can be employed to detect substances in various media. In the times of old, chemists invented methods such as titration and colorimetry which have been improved over the years yielding precise, accurate, valid and reliable results.
When chemical analysis are conducted, are the results obtained accurate? How can we say if they are or not? This investigation involves using different analytical techniques to determine the concentration of the same variable, copper (II) ions, and comparing the effectiveness of these techniques.

Aim **To find the concentration of Cu^{2+} ions using different quantitative analytical methods, and comparing their relative accuracy, precision and reproducibility of the results.**

The medium containing the copper ions is a solution of copper sulphate. This solution (unknown concentration) is then tested using each of the methods below to determine a value for the concentration:

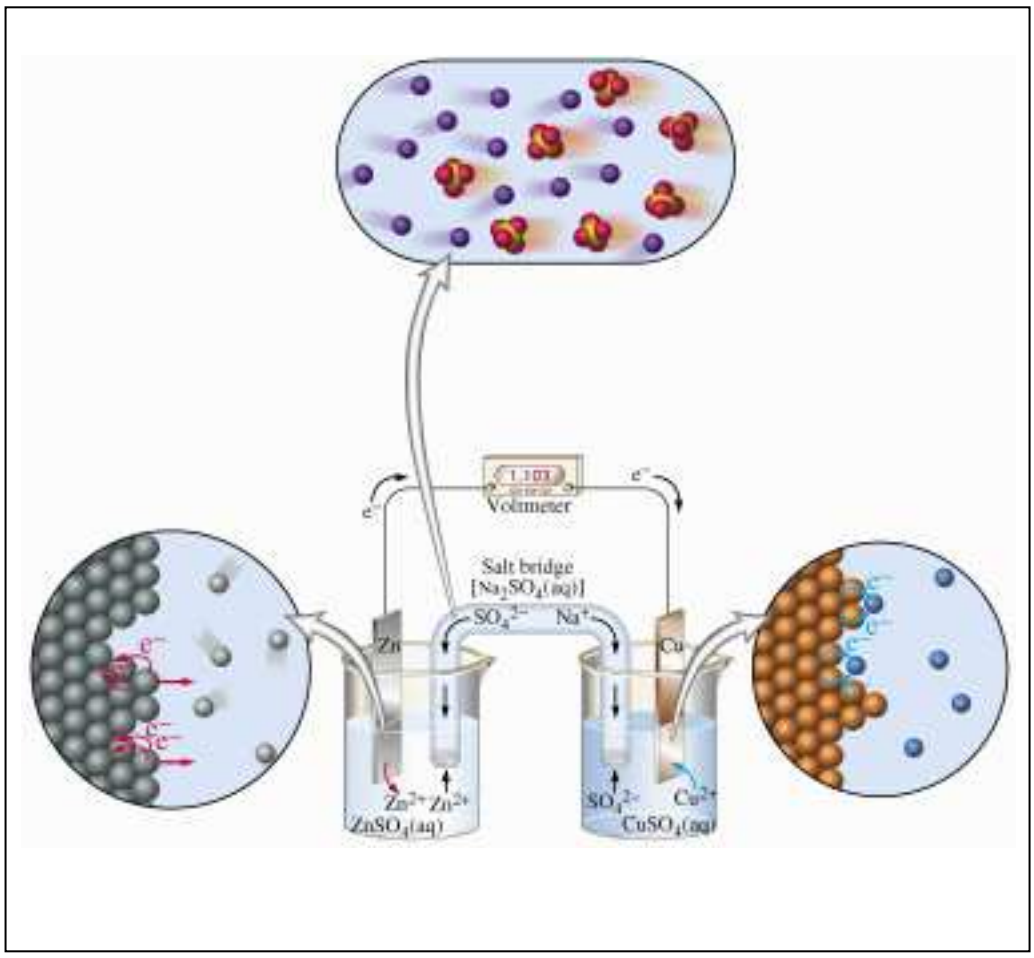
I. **Electrochemical cell analysis**
II. **Colorimetric analysis**
III. **Redox titration**
IV. **Complexiometric titration**
V. **Gravimetric analysis**
VI. Ion exchange followed by acid-base titration

Synoptic Coverage

AS	A2
• Redox (M - P2)	Transition metals (SS – P3)
• Chemical equilibrium (A –P2)	Electrochemical cells (SS – P3)
• Moles, concentration, volume (EL, DF,M,A – P1 & 2)	Complex ions (SS – P3) Colorimetry (SS – P3)
• Volumetric analysis (EL,DF – P1)	Electrode potentials (SS – P3)
• Half equations (M,A – P2)	Nernst equation
• Oxidation numbers (M – P2)	Ion Exchange (AA – P4)
• Serial dilution	

Electrochemical analysis

Electrochemistry is based solely on redox reactions of the transfer of electrons, from the less positive to the more positive terminal. An electrochemical cell is composed of two half-cells connected by electric wires and a salt bridge. A half-cell simply consists of a salt solution of a particular metal ion and a strip of the same elemental metal dipped into the solution. These are connected by electric wires to a high resistance voltmeter and a salt bridge consisting of a strip of filter paper soaked in potassium nitrate.



Copper/zinc cell

[1] www.vss.psu.edu.../electrochemistry.pdf

The system allows current flow, as the salt bridge contains the ions which carry the current. Let us look at the cell diagram of the copper/zinc cell as above:

$$\mathbf{Cu^{2+}, Cu \; \| \; Zn, Zn^{2+}}$$

The more positive and less positive terminals are determined by the potential difference given when each of the half-cells is set up with a standard hydrogen half-cell called the **Hydrogen reference cell**. All half-cells have standard conditions of 298 K temperature, 1 atmosphere pressure (101.3 kPa) and a solution concentration of 1 mol dm^{-3}.**The standard electrode potential** of half-cells can be outlined as the potential difference between it and the hydrogen reference cell, and the signs allocated to these values indicate whether they are at a more or less positive potential then the reference cell.
In this investigation, the copper half-cell is more positive than the zinc half-cell.

At the less positive terminal:

$$Zn_{(S)} \longrightarrow Zn^{2+}_{(aq)} + 2e^- \quad E^0_{Cell} = -0.76 \text{ V} \quad \textbf{(oxidation)}$$

At the more positive terminal:

$$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)} \quad E^0_{Cell} = +0.34 \text{ V} \quad \textbf{(reduction)}$$

These oxidation and reduction reactions take place to produce a voltage for the electrochemical cell, which is found by the equation:[2]

$$\mathbf{E_{Cell} = E_{Reduction} - E_{Oxidation}}$$
$$= +0.34 - (-0.76)$$
$$= \mathbf{+1.10 \text{ V}}$$

This is the potential difference of the copper/zinc cell in which the concentrations of the ions are standard (1mol dm^{-3}).
The potential difference or **voltage** of an electrochemical cell is a direct relationship of the concentrations of the solutions incorporated in the cell. Changes in the concentration affect the voltage of the system and therefore this investigation comprises of determining the voltages of different concentrations of copper(II)sulphate solutions, and finally the unknown concentration solution, to construct a calibration graph of voltage against concentration from which the concentration of the unknown can be extrapolated.

[2] Salterss Advanced Chemistry series, Chemical Ideas page 214

This method of analysis investigates the use of electrode potentials to determine the concentrations of metal ions in solution. In this case, the unknown concentration of Cu^{2+} metal ions in a solution of copper(II) sulphate. There are two alternatives to this:

I. Constructing a copper(II) ion concentration/cell potential calibration curve. A range of known concentrations of copper(II) sulphate solution is prepared, and the E_{Cell} values are plotted. The unknown concentration solution can then be found by interpolating the graph and reading off the concentration value.
II. Alternatively, calculations can be done using the Nernst equation, 'which is derived from the free energy and 2nd law of thermodynamics'[3]:

$$E_{Cell} = E^f - \left(\frac{RT}{nF}\right) \ln Q$$

Apparatus

- High resistance voltmeter
- 1 strip of copper metal (10cm long by 4cm wide)
- 1 strip of zinc metal (10cm long by 4cm wide)
- Chromatography paper
- Piece of sand paper
- Beaker ($250cm^3$) x2
- electric leads with crocodile clips x2

Materials

- copper(II) sulphate solution (of unknown concentration)
- 110g potassium nitrate
- 287.54g zinc sulphate crystals
- 249.68g copper(II) sulphate crystals

Justification of apparatus

The high resistance voltmeter is used to ensure that no current flows through and an accurate voltage is put across.

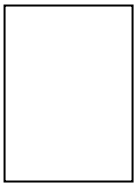
A new salt bridge is to be made for each testing to prevent any contamination.

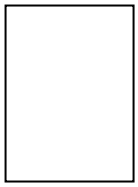
Sand paper is important as it is used to clean off the oxide layer on the metal strips, as they should really have a chemically clean surface otherwise leading to inaccurate results.

[3] www.york.ac.uk/org/seg/salters/ chemistry/OCR_PDFS/INVESTIGATION2.PDF

The 250cm^3 beakers are the standard apparatus used in electrochemical cells.

Risk Assessment





Always wear eye protection always wear gloves

Potassium Nitrate: Danger: **OXIDISING AGENT**[4]

Contact with other material may cause fire. Harmful if ingested, inhaled or absorbed through skin. Causes irritation to the eyes, skin and respiratory tract.

If ingested: induce vomiting immediately, seek medical attention
If spilt on skin: immediately flush skin with plenty of water for at least 15 minutes. Remove nay contaminated clothing. Seek medical attention if irritation persists.
If splashed in eyes: immediately wash eyes with plenty of water for at least 15 minutes, lifting upper and lower lids occasionally. If irritation persists, seek medical attention.

Disposal: dispose of according to the law. Flush down the drain with copious amounts of water.

Zinc Sulphate: **HARMFUL**[5]

May cause mild irritation to the eyes and skin, potential environmental hazard.

If ingested: dilute the stomach contents with 2-4 cupful's of water or milk. Do not induce vomiting . seek medical attention if irritation persists.
If spilt on skin: immediately flush skin with plenty of water for at least 15 minutes. Remove nay contaminated clothing. Seek medical attention if irritation persists.
If splashed in eyes: immediately wash eyes with plenty of water for at least 15 minutes, lifting upper and lower lids occasionally. If irritation persists, seek medical attention.

Disposal: do not throw concentrated solutions down the drain. Zinc is a metal poison to plants and effects the environment. If zinc is not concentrated, then

[4] www.jtbaker.com/msds/englishhtml
[5] www.products.tech.cominsco.com

flush down the drain with copious water.

Copper(II) sulphate : **HARMFUL**[6]

If ingested: rinse mouth with water, and then consume a copious amount. If irritation persists then seek medical attention.
If splashed in eyes: rinse eyes gently with running tap water. If irritation persists seek medical attention.
If spilt: no appreciable hazard to clothes. If spilt in laboratory then make sure the area washed with water and cleaned up.

Disposal: down sink with copious amounts of water, as copper is a toxic metal to plants and inhibits growth, therefore harming the environment.

Preparation of the solutions[7]

Copper(II) Sulphate calibration solutions

CALCULATIONS: 1 mol dm^{-3} = 63.5 + (16 x 4) + 32.1 + (5x18) = **249.68g** of $Cu(II)SO_4$

I. Weigh out about 249.68g of copper(II) sulphate crystals on an electric balance, using a weighing boat.
   This can be carried out by weighing the boat first and noting down the weight, then the mass of the crystals + boat, finally subtracting the two to get the mass of the crystal.
II. Transfer crystals to a 1000 cm^3 beaker and add water to dissolve the crystals, (gently crushing with a glass rod) until all the crystals have dissolved. Make sure all washings of the boat are transferred.
   This amount of solid will take some effort and time to dissolve so a magnetic stirrer would be appropriate.
III. Transfer this mixture and all washings to a 1dm^3 volumetric flask.
IV. Finally, make up the volume of the flask up to the line using distilled water.
V. Stopper the flask and mix well.
   An accurate technique is to invert the flask 20 times, and after each inversion, rotate the flask. This ensures a homogenous solution and minimises inaccuracy.
VI. Label this flask copper(II) sulphate stock solution.

All the calibration solutions must be diluted from the 1mol dm^{-3} stock solution and made up to 1000 cm^3 , rather than 100cm^3, as working in litres has a lower

[6] Hazcards
[7] preparations of all solutions in this method are from Titrimetric Analysis for A and S Levels- JG Stark – ISBN: 0-7195-2446-6

percentage error. The amount of the solution wanted can then be transferred to bottles and stocked up.

This is done as follows:

0.1 mol dm^{-3} = withdraw 100cm^3, using a volumetric pipette, of the standard copper sulphate solution and transfer to a 1dm^3 flask. Make up to the line using distilled water.

0.01 mol dm^{-3} = withdraw, from the 0.1 solution using a volumetric pipette, 100cm^3 and transfer to a 1dm^3 flask. Make up to the line using distilled water.

0.001 mol dm^{-3} = withdraw, from the 0.01 solution using a volumetric pipette, 100cm^3 and transfer to a 1dm^3 flask. Make up to the line using distilled water.

0.0001 mol dm^{-3} = withdraw, from the 0.001 solution using a volumetric pipette, 100cm^3 and transfer to a 1dm^3 flask. Make up to the line using distilled water.

0.00001 mol dm^{-3} = withdraw, from the 0.001 solution using a volumetric pipette, 100cm^3 and transfer to a 1dm^3 flask. Make up to the line using distilled water

Zinc Sulphate

CALCULATIONS: M_r = 287.54.
1 mol dm^{-3} = 161+ (7x18) = **287.54g**

I. Weigh out accurately 287.54g of zinc sulphate crystals in to a 1000cm^3 beaker.
II. Add water and dissolve the crystals, gently crushing with a glass rod. Stir well. Make sure all washings of the boat are transferred.
This amount of solid will take some effort and time to dissolve so a magnetic stirrer would be appropriate.
III. Transfer this mixture to the 1dm^3 flask along with the washings. Make up to the line using distilled water. Stopper the flask and mix well via the inverting technique.
IV. Label this 1M Zinc Sulphate stock solution.

Potassium Nitrate(V)

CALCULATIONS: M_r = 101.
1 mol dm^{-3} = **101g**
So 4 mol dm^{-3} = 101 x 4 = **404 g**

The amount needed for a 250 cm^3 volumetric flask is a quarter of the mass of solid. So for a 4 M solution in a 250cm^3 volumetric flask = $\frac{404}{4}$ = **101g of KNO_3**

For a saturated solution, a little more excess of the solid id needed, therefore **110g**, in total, of the solid is needed.

I. Weigh out accurately 110g of potassium nitrate crystals in to a small beaker.
II. Add water and dissolve the crystals, gently crushing with a glass rod. Stir well.
III. Place the beaker onto a hot plate and stir.
IV. Transfer this mixture to the 250 cm^3 flask along with the washings. Make up to the line using distilled water. Stopper the flask and mix well via the inverting technique.
V. Transfer the solution to a bottle and allow to cool, this allows for crystallization to occur.
VI. Label this 4M Potassium Nitrate (saturated)

The Electrochemical method

I. Pour about 200cm^3 of one of the calibrated solutions of copper sulphate into a 250cm^3 beaker (start with the lowest concentration). Make sure the beaker is first rinsed with distilled water and then with the calibrated solution to undergo analysis.
II. In the second beaker, pour the same amount of the standard zinc sulphate solution.
III. Obtain the 2 metal strips and clean with the sand paper.
IV. Place the copper strip into the copper half-cell and the zinc strip into the zinc half-cell.
V. Bend the extruding tip of the copper strip into a hook shape and hook over the rim of the beaker. Clip this firmly into place with the crocodile clip of one electric lead.
VI. Carry out the same procedure for the zinc half-cell.
VII. Attach the ends of both electric wires to the correct terminals on the voltmeter.
VIII. Obtain a clean beaker and rinse with distilled water, now pour enough potassium nitrate solution into it to allow submersion of the filter paper.
IX. Cut some chromatography paper into a strip 5 cm wide and 20cm long. Dip this into the potassium nitrate solution and allow for total saturation. Make sure the switch on the voltmeter is off before going any further.
X. With protective gloves on, transfer the salt bridge to the set up

apparatus, dipping one end of the bridge half way into one beaker and the same for the other end of the bridge.

XI. Now switch on the voltmeter and observe the reading. Record on a suitable table

XII. Repeat the whole procedure for each of the calibration solutions.

XIII. When conducting the analysis for the unknown sample, pour a new solution of zinc sulphate into the beaker, clean the zinc and copper metal strips, and rinse the copper beaker with the unknown solution before testing.

Modifications to the method

Initially, it was planned to have a calibration range of 0.40-0.80 mol dm^{-3}, in intervals of 0.05. The preliminaries showed that the voltmeter was not sensitive enough to discriminate between the narrow range and many of the voltage readings were the same (see the results table for evidence).
To overcome this problem, the calibration solutions were scrapped and a new range of **0.10**, **0.01**, **0.001**, **0.0001**, **0.00001** mol dm^{-3} were made. This gave promising and more accurate, precise results in the range of 1.01-1.08 V.
The unknown concentration solution was also diluted down from 0.6(approximate concentration) to 0.006 mol dm^{-3}. This factor of dilution was chosen because the approximate concentration would lie near the centre of the range.

Implementation

Results Table for Electrochemical analysis

Range of calibration solutions is from **0.40 – 0.80 mol dm^{-3}**

	Calibration solutions of known concentration (mol dm^{-3})									
	0.40	0.45	0.50	0.55	0.60	0.65	0.70	0.75	0.8	**Unknown**
Voltage (V)	1.06	1.06	1.07	1.07	1.07	1.08	1.08	1.09	1.10	**1.07**

The above table shows that some values of different concentrations have the same value for the voltage. This is because the voltmeter cannot discriminate between concentrations of a narrow range.

The second results table is for the modifications made to the method.

	Calibration solutions of known concentration (mol dm^{-3})					
	0.10	0.01	0.001	0.0001	0.00001	**Unknown**
Voltage (V)	1.080	1.060	1.050	1.030	1.010	**1.055**

Analysis of results

The results for the electrochemical analysis are to be either plotted onto a calibration graph or worked out using the Nernst equation. I will consider the calibration graph. The voltages of each known concentration calibration solution can be plotted against the corresponding concentration, voltage (V)/ concentration (mol dm^{-3}) and the concentration can be found by interpolating the graph and reading off the concentration value. The calibration graph 1 of known concentration solutions against voltage shows that reading across from the **1.055 V** value and down to the concentration axis, the concentration reads **0.005 mol dm^{-3}**. However, this is not the final concentration value. Since dilutions were made, the concentration value must be multiplied back up again.

Dilution $= \frac{0.6}{100}$ (approximate concentration)

$= 0.006$ mol dm^{-3}

Multiplying back by one hundred = 0.005 (the calibration graph value)
x
100 (diluting factor)

$= \mathbf{0.50\ mol\ dm^{-3}}$

The expected value can be calculated using the Nernst Equation. For example, the expected value for the 0.1 mol dm^{-3} concentration solution of copper(II)sulphate is:

$$\mathbf{E_{CELL} = E_{CELL} - \left(\frac{R\,T}{N\,F}\right) \ln \left(\frac{a_{red}}{a_{ox}}\right)}$$

$$E_{CELL} = 1.10 - \left(\frac{8.314\ T}{2 \times 96\,496}\right) \ln \frac{[Cu^{2+}]}{[Zn^{2+}]}$$

$$E_{CELL} = 1.10 - [0.00004308\ T]\ \ln \frac{[Cu^{2+}]}{[Zn^{2+}]}$$

Rearranging the equation by using logarithm, and because $[Zn^{2+}]$ is 1 mol dm^{-3} throughout, the equation becomes:

$$\mathbf{E_{CELL} = 1.10 + [0.00004308\ 298]\ \ln\ [Cu^{2+}]}$$

= 1.10 + (0.01283784 x -1)
= 1.10 + -0.01283784)
= **1.08 V** (omitting subsequent significant figures)

The expected voltage value reflects the experimental value, 1.08 V, of the voltage across the cell of copper(II)sulphate concentration 0.1 M.

Conclusions

The actual concentration of the supplied copper sulphate solution, the "unknown", was **0.60 mol dm^{-3}**. The results of this electrochemical analysis found the concentration to be **0.50 mol dm^{-3}**. A concentration value which has a 1% error to the actual concentration value is considered highly accurate. The result from this analysis was 0.10 mol dm^{-3} lower than the actual concentration.
The aim of this investigation was to determine which analytical technique is most accurate, precise, and gives rise to reproducible results. These are the three aspects of this analytical technique which must be considered.

To begin with, the extent of **precision** can be seen by considering the range in which the voltages of the calibration solutions of known concentration fall in. Theoretically, the range in which the calibration solutions that were employed in the modified trial should be between **0.96 – 1.10 V**. The range in which the experimental results I found was **1.01 – 1.08 V**. This is not as wide as the theoretical range, however considering the limited nature of this analytical technique and the fact that the results were taken in a school laboratory, it does constitute to a substantial degree of precision. Another reason why the experimental voltage values do not span the full range could be due to the temperature of the system. The first trial gave rise to many anomalous results. As stated earlier, the voltmeter was not sensitive enough to discriminate between such a narrow range of 0.40 – 0.80 mol dm^{-3}. Also, since it was the first trial there could have been other sources of error such as in the cleaning of the electrodes after each solution was tested and also any contamination of the solutions while the electrodes were being cleaned.

The second trial was not a **replication** of the first trial; however the method was carried out exactly as planned both times. The electrochemical analysis was not replicated a further time because firstly, the Nernst equation calculation illustrated that the theoretical expected value of the 0.1 mol dm^{-3} was indeed the value obtained from the experiment. This allows us to assume that the calculations of the subsequent dilutions would also produce the expected values and secondly, because the making of the solutions and dilutions, and the actual experiment itself is a time-consuming process and time was a major factor in this investigation as there are many other analytical techniques which needed to be conducted in a short period of time. However, had a replication been carried out and if there were slight variations in the molarities of the solutions then this would not have major effects on the voltages in terms of variation in the experimentally determined voltages and would not affect the precision of the technique.

Making solutions of different concentrations by serial dilutions gives rise to more **accuracy** than making each solution separately. This is because the subsequent dilutions are direct divisions and there is less room for error, taking into account the pipettes were used correctly and accurately. The solutions that were made were all made up to 1 dm^3 instead of 100cm^3 which further ensures a higher degree of accuracy of the results.
The calibration graph for this analysis reads that the concentration is 0.005, which when multiplied back (reverse of the dilution), is **0.50 mol dm^{-3}**. The difference between this and the actual concentration of the unknown solution is 0.10 mol dm^{-3}, which is not very accurate. From the evaluation, we have determined the percentage error of the variance between the actual concentration of the "unknown" and the experimentally determined value and this error is **16.7%.** This is very high. Looking at the result, it is only 0.10 mol dm^3 lower than the actual concentration and the variation does not seem very large. However on a critical level, the error is too great to consider it accurate. The line of best fit is highly significant when it comes to reading off the concentration value because it can give rise to inaccuracy. The major factor to consider is the drawing of the line. The line must touch as many of the points as possible and because the results are experimental, slight fluctuations of the points on the graph are to be expected, if not a distinct curve. These slight variations mean that the accuracy of the line is subjective, which in turn may affect the determination of the value of the concentration.

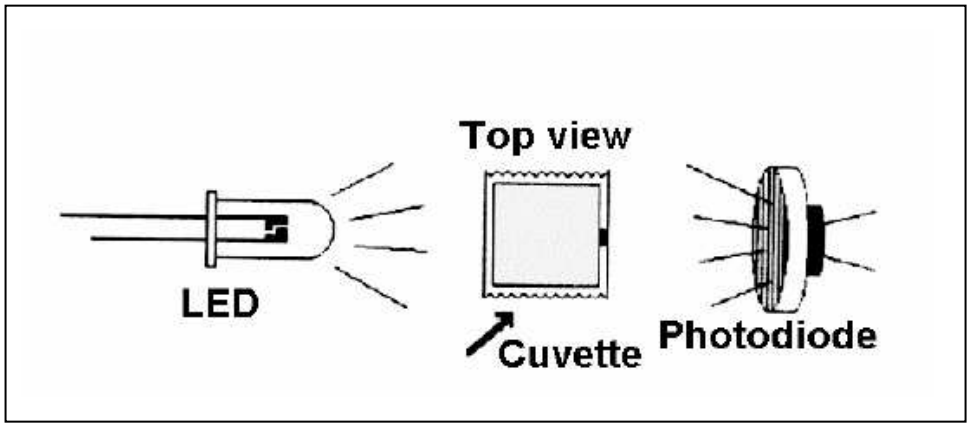
The major limitation of the experiment was the accuracy. More time could have been devoted to a slower pace of carrying out the procedure but as discussed below, this could not have been possible.
The time limit was a constraint. If there was more time then the experiment could have been repeated at least three times. Also, more attention could have been given to the cleaning of the apparatus and electrodes and the solutions could have been made up at the same time each trial is to be conducted, as these reduce the chances of contamination. These measures were not possible to carry out due to the fact that there were more techniques to be analyzed in a short period of time.

Evaluation

As the temperature increases, the electrode potential of the cell decreases and if there were any increase in temperature while the experiment was being carried out then this could have reduced the range extent of the cell voltages of the calibration solutions.

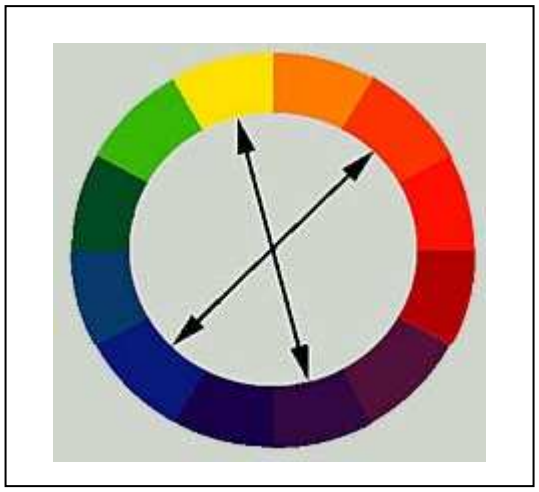
Colorimetry Analysis

Colorimetry apparatus is used when trying to determine the concentration of ions in a coloured solution. In this case, the concentration of copper ions in a **blue** solution of copper(II)sulphate.
The colorimeter works by placing a cuvette containing the copper(II) sulphate solution into a slot in the apparatus. A narrow beam of light is then passed through the solution, via a filter, and any transmitted light is detected by a photocell. The reading comes up on the transmittance/absorbance meter and read off accordingly.



[8]

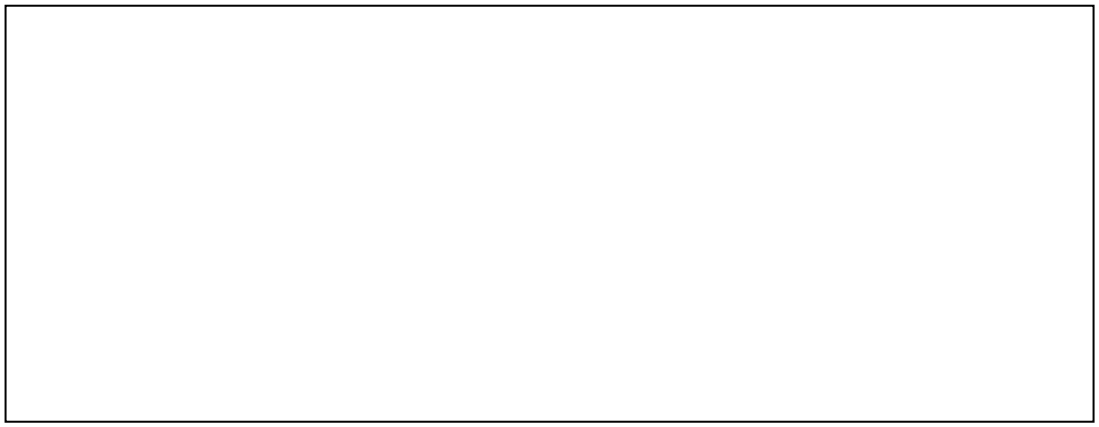
The filter that is used is determined by a complementary colour wheel.


[9]

The filter selected should be that which maximises the amount of light that can be absorbed by the coloured solution. For instance, a solution which absorbs wavelengths of orange light will be coloured blue. Therefore the solution will absorb orange light more strongly when using an orange filter. The colour wheel above indicates that orange is the complementary colour of blue. Alternatively,

[8] www.cma.science.uva.nl..../do358.pdf
[9] http://hort.ifas.edu....htm

each filter can be tested in turn to see which gives the highest transmittance/absorbance reading.
In the case of copper (II) sulphate solution, the copper^{2+} ions are a blue colour when water molecules complex with it. So, an orange filter will be used.
The concentration of copper ions can be found by constructing a calibration graph of a range of known concentrations, and then incorporating this into the line of best fit. The concentration can be read off either using the absorbance or the transmittance. Initially I will be working with the transmission reading, because transmission is easier to read off the colorimeter. However, because absorbance is proportional to the concentration, the transmission values will be converted to absorbance values.



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Transmittance is the amount of light that penetrates a solution. Transmittance (T) can be worked out as the ratio of the intensity of the light transmitted (It), and the initial intensity of the beam of light (Io) as shown by the formula: (ref here)

$$T = \frac{It}{Io}$$

An additional measurement is related to colorimetric analysis which is absorbance (A). It is assumed that the two variables have a **simple** inverse relationship proportional to each other, that is, as the transmittance of light by a solution increases the amount of light that is absorbed is expected to decrease accordingly.
In fact the relationship is actually logarithmic (base 10) as well as inverse:

$$A = \log \frac{1}{T}$$

10

On the other hand, transmittance is not proportional to the concentration of the solution. However it can be converted into absorbance using a calculation, this is proportional to the concentration of the solution and is derived using the following formula:

$$A = 2 - \log_{10} \%T$$ [11]

This illustration shows the inverse relationship between transmittance and absorbance, and expresses that e.g. if all the light passes through a solution, then there is no absorbance and results in 100% (T) and 0% (A). On the other hand if no light is being transmitted then it means 0% transmittance and infinite absorbance.

Apparatus

- Colorimeter
- Cuvettes x2 (1 for the blank, 1 for the calibrations)
- Boiling tubes x10 and rack
- rubber bung x10
- clamp and stand x2
- glass rod
- volumetric flask (1dm^3, 10cm^3, 50cm^3 and 250cm^3)
- beaker (1000cm^3)
- labels

Materials

- 249g copper(II) sulphate crystals
- Unknown concentration solution of copper(II)sulphate.

Justification of apparatus

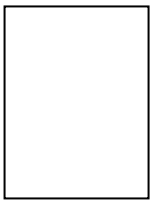
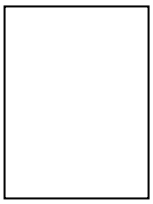
2 cuvettes, one for the sample solutions should be used and one for the blank as this will reduce the errors and to avoid contamination, after each calibration solution has been analysed, the cuvette should be washed with the next solution to be analysed.

The wide range of volumetric flasks are needed to carry out measuring and transferring of the stock solutions to obtain the dilution solutions.

[11] all the log calculations are from http://www.bio.davidson.edu/Courses/Bio111/Bio111LabMan/Lab%201.html

Labels are very important when dealing with a large number of bottles and tubes, to reduce any befuddlement.

Risk Assessment[12]

 Eye protection  gloves

Preparation of the solutions[13]

Copper(II) Sulphate calibration solutions

CALCULATIONS: 1 mol dm^{-3} = 63.5 + (16 x 4) + 32.1 + (5x18) = **249.68g** of $Cu(II)SO_4$

VII. Weigh out about 249.68g of copper(II) sulphate crystals on an electric balance, using a weighing boat.
This can be done by weighing the boat first and noting down the weight, then the mass of the crystals + boat, finally subtracting the two to get the mass of the crystal.
VIII. Transfer crystals to a 1000 cm^3 beaker and add water to dissolve the crystals, (gently crushing with a glass rod) until all the crystals have dissolved. Make sure all washings of the boat are transferred.
This amount of solid will take some effort and time to dissolve so a magnetic stirrer would be appropriate.
IX. Transfer this mixture and all washings to a 1dm^3 volumetric flask.
X. Finally, make up the volume of the flask up to the line using distilled water.
XI. Stopper the flask and mix well.
An accurate technique is to invert the flask 20 times, and after each inversion, rotate the flask. This ensures a homogenous solution and minimises inaccuracy.
XII. Label this flask copper(II) sulphate stock solution.

A range of calibration solutions ranging from 0.01 – 0.1 $moldm^{-3}$ would need to be prepared because preliminaries showed that the 0%transmission is obtained with higher concentrations. So a series of dilutions ranging from 0.01 to 0.1M, in

[12] All hazards and safety procedures are from hazcards.
[13] All solutions prepared in this method are from Titrimetric Analysis for A and S Levels- page 11 onwards- JG Stark – ISBN: 0-7195-2446-6

intervals of 0.1 will need to be prepared in order to obtain any readings.
A 0.1 mol dm^{-3} solution needs to be prepared to make easier subsequent dilutions.
100 cm^3 of the 1M solution is pipetted out and transferred to a 1dm^3 volumetric flask. Distilled water is then added and made up to the line.
All the calibration solutions must be diluted from the 0.1 mol dm^{-3} stock solution and made up to 1000 cm^3 , rather than 100cm^3, as working in litres has a lower percentage error. The amount of the solution wanted can then be transferred to boiling tubes.This is done using the table below.

Volume of Cu(II)SO_4 solution (cm^3)	**Volume of distilled water (cm^3)**	**Concentration of the copper calibration solution (mol dm^{-3})**
100 from the 0.1 M	900	**0.01**
200 from the 0.1 M	800	**0.02**
300 from the 0.1 M	700	**0.03**
400 from the 0.1 M	600	**0.04**
500 from the 0.1 M	500	**0.05**
600 from the 0.1 M	400	**0.06**
700 from the 0.1 M	300	**0.07**
800 from the 0.1 M	200	**0.08**
900 from the 0.1 M	100	**0.09**
100 from the 1M	900	**0.10**

The colorimetry method

Making the calibration curve

I. Before analysing the unknown Cu(II) sulphate solution, a calibration graph/curve, consisting of transmission (%) against concentration of Cu^{2+} ions, must be constructed.
II. Obtain two cuvettes, one for the blank and one for the calibration test solution.

The blank is usually the solvent being used in the calibration solution.

III. Start with the lowest concentration of the calibration solution (0.1 %). Pipette the solution into the cuvette about 2/3 of the way. This ensures that the photocell 'sees' the solution.

IV. The same procedure is to be done for the blank cuvette, this time using the distilled water.
Note: When filling the cuvette with each calibration solution, the cuvette must be rinsed with the solution to undergo analysis.

V. Switch the colorimeter on, let it warmup for at least 5 minutes.
To obtain maximum transmission, select the appropriate filter using the complemetary colour wheel.

VI. Place the blank solution cuvette into the colorimeter and cover with a box to prevent external light entering.
Press the zero button. Be careful to face the clear side towards the photodiode and light source.
Always take precaution to handle cuvettes with the frosted side, if not then the clear side becomes contaminated and this leads to inaccurate and unreliable results.

VII. Check that the meter pointer reads either 100% transmission or 0% absorbance.

VIII. The cuvette must be covered with a small box to prevent any external light from entering or else this would falsify the results.
Note: make sure this procedure is repeated before every calibration solution to undergo analysis.

IX. Remove the blank cuvette and replace with the calibration solution. Record the absorbance/transmission reading.

X. Repeat steps 3-7 for each of the calibration solutions and plot the readings on the graph of transmission/absorbance against concentration.
The calibration graph has now been constructed.

XI. Repeat steps 3-7 for the unknown concentration of copper(II) sulphate solution.

XII. Determine the concentration by extrapolating from the graph, by reading across the absorbance/transmissin value, and then down to the concentration value.

XIII. If the unknown concentration solution does not give a transmission reading i.e. if the solution is too concentrated for the light to pass through, then a dilution is in order.
When interpolating the unknown sample on the calibration graph, the concentration reading obtained must be multiplied back up by the factor it was diluted by. E.g. if the dilution was a tenth, then the concentration reading must be multiplied by 10.

Modifications to the method

The highest and lowest concentration of the range of calibration solutions were analysed by the colorimeter and I found a range of at least 60% between the two. This ensures that the range is wide enough for the unknown sample to fall somewhere between the centre of the range.
The unknown sample, when tested, gave 0% transmission and so a dilution of 25cm^3 of the solution up to 50cm^3 was conducted. This still gave 0% transmission and so another dilution was done taking 10 cm^3 and diluting up to 100 cm^3. This reading gave 30% transmission which lays near enough the centre of the range.

Implementation

Results Table for Colorimetric analysis

Filter : **Orange**

	Calibration solutions of known concentration (mol dm^{-3})										
Test 1	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.10	**Unknown**
Transmission (%)	78	63	52	44	38	32	26	22	18	16	**30**

	Calibration solutions of known concentration (mol dm^{-3})										
Test 2	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.10	**Unknown**
Transmission (%)	78	63	52	44	38	32	26	22	18	16	**30**

Analysis of results

Now that the results have been accumulated, the % transmission values of the calibration solutions can now be plotted onto a calibration curve of transmission/concentration.

(see calibration graph1 on next page)

Interpolating the **test 1** graph shows that going across the graph at **30%** transmission for and then down after reaching the curve, it reads off at **0.063** mol dm^{-3}. This is not the final concentration value and, due to 1/10 dilution of the unknown solution, it must be multiplied back by ten to reach the original value:

Dilution $= \frac{0.6}{10}$ (approximate concentration)

$= 0.06$ mol dm^{-3} (this molarity enables readings)

Multiplying back by a tenth = 0.063 (the calibration graph value)
x
10 (diluting factor)

= **0.63 mol dm^{-3}**

The same procedure was carried out for the **test 2** and the concentration came to be:

0.063 (the calibration value)
x
10 (diluting factor)

= **0.63 mol dm^{-3}**

The transmission values for the calibration solutions produced a curve. There is however a certain amount of inaccuracy which occurs when drawing the curve. Therefore, incorporating logarithm and using the formulae:

$$\mathbf{A = 2 - \log_{10} \%T}$$

We can convert each of the transmission values into absorbance values which in theory should give a linear regression. Since the data obtained are experimental, the line is not expected to be precisely straight but it is enough to accurately read values off the graph.

Test 1

Calibration solutions of Unknown concentration	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.10	unknown
Transmission	78	63	52	44	38	32	26	22	18	16	**30**
Absorbance	**0.108**	**.201**	**.284**	**.357**	**421**	**.495**	**.585**	**.658**	**.745**	**.796**	**0.523**

Test 2

Calibration solutions of Unknown concentration	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.10	unknown
Transmission	78	63	52	44	38	32	26	22	18	16	**30**
Absorbance	**0.108**	**.201**	**.284**	**.357**	**.421**	**.495**	**.585**	**.658**	**.745**	**.796**	**0.523**

The **test 1** graph for the calibration log absorbance values shows that reading across from the unknown concentration absorbance value, the concentration is read as 0.063 mol dm^{-3}. The same calculations as with the transmission values have to be conducted due to the procedural dilution, hence multiplying back up by ten gives the concentration to be **0.63** mol dm^{-3}.

The **test 2** graph also undergoes the same procedure of interpolating and calculating to give the concentration as **0.63** mol dm^{-3}.

(see calibration graph 2 of log absorbance values)

Summary of results for transmission calibration graph

Concentration (mol dm^{-3})	
Test 1	Test 2
0.63	0.63

Summary of results for log absorbance calibration graph

Concentration (mol dm^{-3})	
Test 1	Test 2
0.63	0.63

Conclusions

It is known from the previous analysis that the actual concentration of the unknown solution is 0.60 mol dm^{-3}. The results from the colorimetric analysis produced values of 0.63 mol dm^{-3} for the concentration of the unknown solution. The aim of this investigation was to determine which analytical technique is most accurate, precise, and gives rise to reproducible results. These are the three aspects of this analytical technique which must be considered.

Firstly, we can consider the extent of the **reproducibility** of the results from this analytical technique. The second trial is an exact replication of the first in terms of the methodology and it gave rise to exactly the same results. Even though time was a constraint in this experiment, it was necessary for the replication to be undertaken as there is a final conclusion to be made on the reproducibility of results of the technique. Colorimetry is a complicated experiment to conduct as the cuvettes have to be handled carefully and the calibration solutions must be accurately made to ensure accurate and correct readings. Taking this into account, we can see that from the results table the solutions that were made up in the second test were of exactly the same concentration as those in the initial test because they gave the same transmission values. This indicates that the solutions made in the second trial were precise.

Now we can analyse the degree of **precision** of the technique. This can be seen by comparing the variance between the results of the two tests. From the results table, we can see that there is no variance between the transmission values of both tests. This concludes that the results obtained within the particular period of time the experiment was conducted are 100% precise in that the technique allows for replications of the experiment to give rise to precise results.

The difference between the actual concentration of the unknown solution and the experimentally determined concentration is 0.03 mol dm^{-3}. A result which differs by only 1% to the actual value constitutes to a very high degree of **accuracy** of the technique. The calibration curve for the transmission values reads that the concentration is 0.63 after multiplying back up (reverse of dilution). Referring to the evaluation, the percentage error between the results and the actual concentration of the “unknown” is **0.15%**. This is not very high, and critically analyzing this value means it is below the accepted 1% of error.
The reason for the absorbance calibration graph was to convert the curve into a line as this is more accurate in determining the concentration. The line is expected to be slightly curved as it is an experiment, however it is linear and this confirms the experimental accuracy of the particular values of the concentrations of the calibration solutions. Both absorbance and transmission graphs read that the concentration for the unknown solution is 0.63. Even though the drawing of the graphs has a certain degree of inaccuracy, unlike the graph in the electrochemistry analysis, the transmission graph drawn in this analysis is accurate to a very high extent because the absorbance graph is completely linear

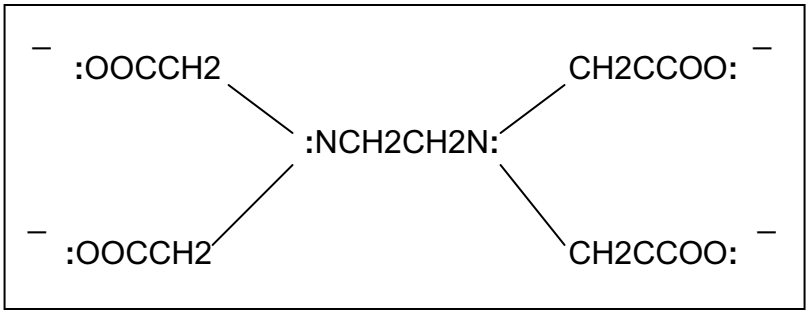
and it shows the same unknown concentration value as the transmission graph. The 0.03 mol dm^{-3} difference must therefore originate from the drawing of the graph which is entirely a subjective measure. The filter that was used was the complimentary colour of the copper sulphate solution and it also gave the maximum transmission reading, so the colorimeter itself could not have given rise to the difference.

This leaves the overall conclusion that the colorimetric method is not accurate enough to get exactly the same value as the actual concentration of the "unknown" solution, however considering the low percentage error of 0.15% means it is relatively accurate. The cuvettes that were used were all the same length and were used in the correct colorimeter as the pathlength affects the transmission value, so this means the major limitation was the drawing of the line, taking into account the making of the solutions were carried out accurately, the colorimeter was used appropriately and the readings were read off as accurately as possible.

Complexiometric Analysis

Complexiometric titration involves titrating metal cations with complexing agents. Take the example of Cu^{2+} ions and EDTA (*ethane diamine tetra ethanoic acid*) usually in its disodium salt ($Na_2C_{10}H_{18}N_2O_{10}$), as it is more soluble than the acid form.

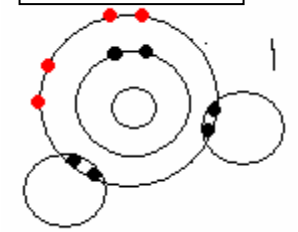
[14]

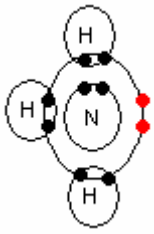


EDTA $^{4-}$ ion

A complex ion has a central metal ion surrounded by a number of other molecules or ions, via dative bonding by a lone pair of electrons. These are called ligands. The most common ligand, when it comes to metal sulphates, is water. Among this are other ligands such as ammonia and chloride ions:

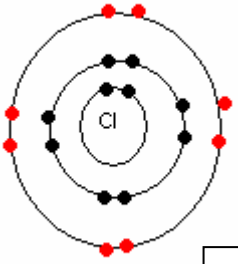
Water





Ammonia

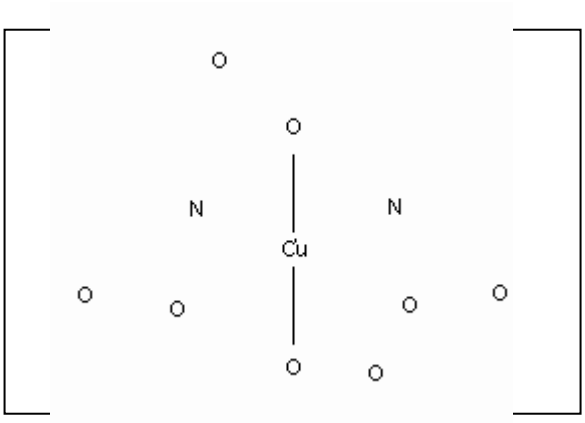
Chloride ion



= electrons involved in complexing

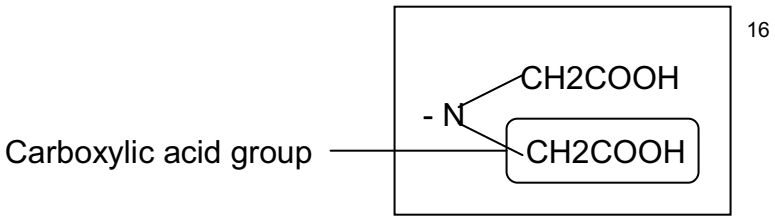
These ligands have active lone pair of electrons in the outer most shell which are involved in complexing. Ligands function as Lewis Bases, in that they are lone pair donors. EDTA is commonly referred to as a chelating agent,

[14] Titrimetric Analysis for A and S Levels- page 54 onwards- JG Stark – ISBN: 0-7195-2446-6



[15]

because of its ability to form more than two bonds with a central metal ion. In fact, EDTA can form 6 bonds with the Cu2+ ion due to the group:



[16]

Where the nitrogen atom and oxygen atoms of the carboxylic acid group can donate a lone pair of electrons to the vacant 4s, 4p and 4d orbitals. The diagram above shows that all the six bonding sites are used up by the EDTA molecule and its cage-like grip, giving the metal ion a coordination number of 6.

EDTA is titrated into a flask containing the unknown concentration of copper(II) sulphate solution, an ammonium chloride buffer at pH10 and an indicator. An ideal colour for the free indicator should be one that is easy to see when free in solution, therefore I have chosen **Fast Sulfon Black**. This is highly coloured and complexes with the Cu^{2+} ions. The deep blue solution, due to the complexed ammonia, turns turquoise at the end-point, which is fairly easy to see.
Once the titration has started the EDTA, due to its higher K_{stab} value of 0.3×10^{16} $mol^{-1}dm^{-3}$, displaces the indicator and binds to the copper ions in a stoichiometric ratio of 1:1, which is why EDTA was chosen as the complexing agent as the 1:1 ratio means it is easy to work with calculations:

$$Cu^{2+}_{(aq)} + (EDTA)^{-4}_{(aq)} \longrightarrow Cu(EDTA)^{2-}_{(aq)} + 2H^{+}_{(aq)}$$

15
16

EDTA forms a more stable complex with the copper than with the Black Sulphon F indicator and liberates it to display its original colour. The free indicator colour appearance means the reaction has come to its end-point and all the metal ions have been complexed with the EDTA.

[17]

$$K_{Stab} = \frac{[Cu^{2+}(EDTA)]^{2-}}{[Cu^{2+}][EDTA^{4-}]}$$

$$= \mathbf{6.3 \times 10^{16}\ mol^{-1}dm^{-3}}$$

$$K_{Stab}\ [\ Cu(NH_3)_4\ ]^{2+} =$$

$$\mathbf{1.3 \times 10^{13}\ mol^{-4}dm^{-3}}$$

EDTA is highly stable complex with the indicator is the reason why I have chosen EDTA as the complexing agent, also it has a higher K_{stab} than the ammonia complex which means displacement is feasible.

Apparatus

- clamp and stand
- pipette x2
- burette
- 250cm^3 conical flask
- 1dm^3 and 250cm^3 volumetric flask
- 100cm^3 and 500cm^3 beaker
- funnel
- weighing boat
- distilled water
- glass rod

Materials

- 1g Fast Sulphon Black
- 1g Murexide indicator
- 'Analar' EDTA (disodium salt)
- unknown concentration of copper sulphate solution
- 143cm^3 concentrated ammonia solution
- 25g ammonium chloride
- 0.1 mol dm^{-3} ethanoic acid
- 0.1 mol dm^{-3} sodium carbonate

[17] Titrimetric Analysis for A and S Levels- page 54 onwards- JG Stark – ISBN: 0-7195-2446-6

Justification of apparatus

Pipettes and burettes are highly accurately calibrated apparatus and are ideal for titration.

EDTA is the ideal complexing agent as the complexes that are formed are almost instantaneous and complex, also reproducible results can be achieved. Also EDTA can be obtained pure to a high extent and for the use as a primary standard it is sufficiently stable.

The ammonium chloride buffer solution is of pH10, because at any value higher than this the copper precipitates out as hydroxides. So the pH at 10 prevents this.

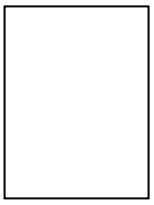
Black Sulphon F is used because the complex it forms with the copper ions has a lower K_{stab} value than the copper-EDTA complex. Therefore this indicator was chosen to make it possible for the reaction to be seen.

The murexide indicator is used for the same reasons as the Fast Sulphon, but in addition, it is easier to see the end-point.

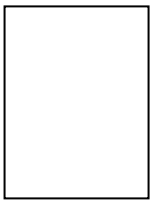
The sodium carbonate and ethanoic acid are of 0.1 molar each because in titrations only small concentrations are used. The two solutions are to remove free minerals in solution.

As with all titrations, the titres should be obtained and averaged. The titres should be concordant to 0.10 cm^3 of each other; otherwise the results cannot conform to accuracy and reliability.

Risk Assessment



Eye protection



Wear gloves

Copper(II) sulphate : **HARMFUL**[18]

No appreciable hazard

[18] www.alsenvitro.com

If ingested: rinse mouth with water, and then consume a copious amount. If irritation
persists then seek medical attention.
If splashed in eyes: rinse eyes gently with running tap water. If irritation persists seek medical attention.
If spilt: no appreciable hazard to clothes. If spilt in laboratory then make sure the area washed with water and cleaned up.

Disposal: down sink with copious amounts of water, as copper is a toxic metal to plants and inhibits growth, therefore harming the environment.

EDTA : **HARMFUL**[19]

Warning! Harmful if ingested or inhaled. Causes irritation to eyes, skin and respiratory tract.

If ingested: The substance has low toxicity but if large amounts are consumed, it may cause a gastric imbalance. So induce vomiting immediately.
Seek medical attention immediately if iriitation resists.
If spilt on skin or lab: Substance is a mild irritant. However immediately flush skin with copious amounts of water for at least 15 minutes. Remove contaminated
clothing. If symptoms persist, seek immediate medical attention.
If splashed in eyes: No major appreciable hazard except that the dust may cause mechanical irritation. Immediately flush eyes with plenty of water for at least 15 minutes, lifting upper and lower eyelids occasionally. If symptoms persist seek immediate medical attention.

Disposal: Whatever is left over, dispose of according to the law. Do not wash down the sink as substance can leak soil and cause environmental disruption.

Fast Sulphon Black: **HARMFUL**[20]

Aggravates target areas and persons with pre existing skin or eye disorders will become more susceptible to symptoms.

If ingested: May cause irritation to respiratory tract. Induce vomiting immediately after giving two glases of water.
If splashed in eyes: Wash with copious amounts of water for at least 15 minutes, lifting upper and lower eyelids occasionally. If irritation persists, seek medical attention.
If spilt on skin: Wash with soap and water. If irritation persists, seek medical advice.

[19] www.jtbaker.com
[20] www.sciencestuff.com

Disposal: To be performed in compliance with local practice and regulations. Do not wash down the sink as this could damage the environment if the substance leaks in to the soil.

Ammonium chloride: **HARMFUL**[21]

Harmful to the eyes.

If splashed in eyes: Wash with copious amounts of water for at least 15 minutes, lifting upper and lower eyelids occasionally. If irritation persists, seek medical attention.
If spilt on skin: Wash with soap and water. If irritation persists, seek medical advice.
If ingested: rinse mouth with water, and then consume a copious amount. If irritation persists then seek medical attention.

Disposal: dissolve in 10 litres of water and wash down the waste drain.

Ammonia solution : **CORROSIVE**[22]

If splashed in eyes: Wash with copious amounts of water for at least 15 minutes, lifting upper and lower eyelids occasionally. If irritation persists, seek medical attention.
If spilt on skin: Wash with soap and water. If irritation persists, seek medical advice.
If ingested: rinse mouth with water, and then consume a copious amount. If irritation persists then seek medical attention.

Disposal: dilute 20 times with water as it is a hazard to the environment, especially the aquatic habitat.

Ethanoic acid : **CORROSIVE**[23]

AVOID ALL CONTACT. If the chemical reaches the eyes then a burning sensation prevails followed by loss of vision.

If spilt in eyes or lab: remove contaminated clothing. Rinse skin and wash eyes with copious amounts of water and soap. Have a shower. Seek medical attention if irritation is experienced.
If ingested: ethanoic acid causes a burning sensation down the alimentary canal and results in diarrhoea. Rinse mouth with plenty of water and consume copious amounts of water. Avoid inducing vomiting and seek medical advice.

[21] hazcards
[22] hazcards
[23] www.chem.ox.ac.uk

Disposal: neutralise the solution under careful supervision and dispose down sink. The solution to be prepared is very dilute (0.1 M) so not much hazard to be expected, however it is important to anticipate the unexpected.

Sodium carbonate: **HARMFUL**[24]

May cause eye burns and is harmful if swallowed, causes irritation to skin and respiratory tract.

If spilt on skin or lab: flush skin with plenty of water and soap. Remove any contaminated clothing and seek medical advice.
If ingested: avoid inducing vomiting, but swallow large amounts of water. Seek medical attention if irritation persists.

Disposal: dispose according to the law.

Murexide indicator: **HARMFUL**[25]

Aggravates target areas and persons with pre existing skin or eye disorders will become more susceptible to symptoms.

If ingested: May cause irritation to respiratory tract. Induce vomiting immediately after giving two glases of water.
If splashed in eyes: Wash with copious amounts of water for at least 15 minutes, lifting upper and lower eyelids occasionally. If irritation persists, seek medical attention.
If spilt on skin: Wash with soap and water. If irritation persists, seek medical advice.

Disposal: To be performed in compliance with local practice and regulations. Do not wash down the sink as this could damage the environment if the substance leaks in to the soil.

Preparation of the solutions[26]

EDTA

CALCULATIONS: 1M solution = 372.2g of EDTA
So 0.1 moldm3 = 372.2/10 = **37.22g** of EDTA

[24] www.chinatrona.com
[25] www.sciencestuff.com
[26] the solutions in this method were from - Titrimetric Analysis for A and S Levels- JG Stark – ISBN: 0-7195-2446-6

I. Fill a weighing bottle with at least 45g of the salt, and dry it at 80C
   This way the EDTA can be used as a primary standard.
II. From this dried mass, weigh out accurately 37.22g of the salt, dissolving it in the minimum amount of water.
III. Transfer to a 1 dm3 flask and make up to the graduation mark using distilled water.
   Make sure all washings are transferred to the flask.
IV. Label this 0.1mol dm^{-3} EDTA.

Black Sulfon F

Since indicators are required in the minimum amount (3-4 drops) to give a good colour, a small amount of the solid is needed. Therefore a $1dm^3$ of 1g of the indicator should suffice.

I. Accurately weigh out 1g of the indicator and transfer to a beaker
II. Add in minimum distilled water and then transfer this to a $1dm^3$ flask along with all the washings.
III. Make up to the line using distilled water.
IV. Transfer to a bottle and label 1% Fast Sulfon Black indicator

Murexide indicator

Because indicators are required in the minimum amount (3-4 drops), a small amount of the solid is needed. Therefore a $1dm^3$ of 1g of the indicator should suffice.

I. Accurately weigh out 1g of the indicator and transfer to a beaker
II. Add in minimum distilled water and then transfer this to a $1dm^3$ flask along with all the washings.
III. Make up to the line using distilled water.
IV. Transfer to a bottle and label Murexide indicator

Ammonium chloride buffer

I. Obtain a clean $500cm^3$ beaker.
II. In a fume cupboard, measure out accurately using a glass measuring cylinder, 143 cm^3 of ammonia solution.
III. Weigh out, in a weighing boat, 22.5g of the ammonium chloride.
IV. Dissolve and make up to $250cm^3$ in a volumetric flask with distilled water.
V. Transfer to a bottle and label Ammonium chloride.

Sodium Carbonate: HARMFUL

CALCULATIONS: M_r of Na_2CO_3 is 106.
1 mol dm^{-3} = 106g of Na_2CO_3
So 0.1 mol dm^{-3} = 106/10 = **10.6g**

I. Heat the sodium carbonate at about 270 C for 45 – 60 minutes, on a clean nickel crucible, on a sand bath.
This is approximately 99.9% pure, and the heating removes final traces of moisture. It is necessary for the procedure to be carried out in the crucible.
II. Allow to cool in desiccators for a bout half an hour. Stir the contents well with a clean nickel crucible.
III. Weigh out accurately about 1.6g of the dry anhydrous sodium carbonate, sealing the weighing bottle during the process to prevent any access of water vapour.
IV. Dissolve in minimum water and transfer to a 250cm^3 flask along with any washings. Make up to the line.
V. Label this 0.1mol dm^{-3} of sodium carbonate

Ethanoic acid : HARMFUL

Since a dilute solution is needed, a 0.1 molar solution will need to be prepared

CALCULATIONS: M_r of ethanoic acid = 60.
1 mol dm^{-3} = 60g
So 0.1 mol dm^{-3} = 60/10 = **6.0g**

I. Dissolve 6.0g of glacial ethanoic acid in water.
II. Transfer the solution to a 250 cm^3 flask along with any washings and make up to the line using distilled water.
III. Label this 0.1 mol dm^{-3} of ethanoic acid (dilute)

The Complexiometric titration method

I. Wash the burette and pipette 3 times with the solution they are to be filled with.
II. Set up the clamp and stand and place the burette firmly in position.
III. Pipette 25cm^3 of the Copper(II)sulphate of unknown concentration from the stock solution into a conical flask.
IV. Place the funnel into position on the burette and carefully pour, filling the burette with standard EDTA solution.
Caution - never pour any chemicals above eye level. If need be, move the whole apparatus to a stool or lower platform for easier access.
V. Run the EDTA solution through the burette, as this ensures a continuous flow

and washes out any residues.

VI. Add three drops of indicator into the conical flask containing the copper sulphate.

VII. Place the conical flask under the jet of the burette, on top of a white tile. The tile makes the colour changes easier to notice and so enabling the detection of a more accurate end-point.

VIII. Run the EDTA from the burette a couple of centimetres at a time simultaneously swirling the flask, until the colour changes to green signalling the near end-point.

IX. Continue adding the EDTA drop-wise until the sudden colour change from green to purplish-blue is observed. This signals the actual end-point.

X. The first titre is the rough. Note down the end-point.

XI. Repeat steps 3-8 to obtain 6 titres.
Make sure, upon reaching the end-point, that the EDTA is added drop-wise for the sudden colour change.
When swirling the flask, take care not to spill or splash any solution as it is hazardous and alters the results.
For each titre, wash out the flask with distilled water thoroughly.

Modifications to the method

Since in titrations, the solutions to be working with have to be of dilute concentrations, the unknown concentration solution of copper(II) sulphate had to be diluted. From the previous colorimetric and electrochemical methods, it was deduced that the concentration of the unknown solution was approximately 0.63 mol dm^{-3}, therefore a dilution down to 0.10 involved:

- Drawing 167 cm^3 of the unknown concentration with a volumetric pipette.
- Diluting to 1000cm^3 with distilled water.

The calculation is dividing the total volume of the solution by the diluting factor:

$$\frac{1000\ cm^3}{6} = \mathbf{167cm^3}$$

(note: to get 0.10 mol dm^{-3} from 0.60 mol dm^{-3} is a diluting factor of 6)

The initial method included the use of the Fast Sulphon Black indicator. When this was added to the tetraaminocuprate(II) ion complex, there was no change in colour, whereas the sources stated there would be. The colour change indicating the end-point can be spotted by turning from deep blue to turquoise. The preliminaries showed that the end-point was very hard to pin-point. There was no clear and distinct sudden change in the colour and the results obtained could be questionable.

The solution to this problem was to use murexide indicator, as it is a tried and tested indicator. The colour change was as follows:

- Copper(II)sulphate + ammonia buffer solution = deep blue solution
- Tetraaminocuprate(II) ion + murexide = no colour change.

- End-point = deep blue – green (near end-point) – spontaneously to purplish-blue (end-point).

This method was actually no different from the previous indicator in terms of the colour change upon adding the indicator. However, the end-point was easier to detect as it suddenly changed from green to purplish-blue.

Implementation

Results Table for Complexiometric titration

Indicator: Fast Sulphon Black- colour change = deep blue to turquoise

	Test						
	Rough	**T1**	**T2**	**T3**	**T4**	**T5**	**T6**
Initial Burette reading (cm^3)	0	0	0	0	0	0	0
Final Burette reading (cm^3)	25.00	24.90	24.80	24.90	24.80	24.70	25.00
Final – Initial (cm^3)	**25.00**	**24.90**	**24.80**	**24.90**	**24.80**	**24.70**	**25.00**

Average Titre = $\frac{\text{6 titres}}{6}$ = $\frac{24.90+24.80+24.90+24.80+24.70+25.00}{6}$ = $\frac{149.10}{6}$

= **24.85**

Indicator: Murexide – colour change = deep blue to green then spontaneously to light blue.

	Test						
	Rough	**T1**	**T2**	**T3**	**T4**	**T5**	**T6**
Initial Burette reading (cm^3)	0	0	0	0	0	0	0
Final Burette reading (cm^3)	25.00	24.80	24.90	25.00	25.00	24.90	24.80
Final – Initial (cm^3)	**25.00**	**24.80**	**24.90**	**25.00**	**25.00**	**24.90**	**24.80**

Average Titre = $\frac{\text{6 titres}}{6}$ = $\frac{24.80+24.90+25.00+25.00+24.90+24.80}{6}$ = $\frac{149.40}{6}$

= **24.90**

Analysis of the results

Since the copper sulphate solution of "unknown" concentration was diluted from 0.60 to 0.10 mol dm^{-3}, and the molarity of the EDTA solution was made 0.1 mol dm^{-3}, In theory, the balanced chemical equation shows that the 1:1 molar ratio means **equal volumes** react completely with each other. If 25.0 cm^3 of the copper(II)sulphate solution was pipetted into the conical flask then **25.0 cm^3** of the EDTA solution should, in theory, react completely with the copper solution. Using the equations below, we can work out the concentration of the copper (II) sulphate solution.

$$Cu^{2+} + (EDTA)^{4-} \longrightarrow Cu(EDTA)^{2-} + 2H^{+}$$

The equation shows that the stoichiometric ratio is 1:1, so 1 mole of the copper ions react with 1 mole of the EDTA solution.

First all the volumes used must be converted to dm^3

dm^3 are standard units used in titration concentration equations.

$$\frac{X}{1000}$$

X ← the volume (cm^3)

1000 ← the conversion of cm^3 to dm^3

Average titre of	
Trial 1	**Trial 2**
$\frac{24.85\ cm^3}{1000\ cm^3}$	**$\frac{24.90}{1000}$**
0.02485 dm^{-3}	**0.02490 dm^{-3}**

Volume of copper sulphate solution pipeted into conical flask

$\frac{25\ cm^3}{1000}$ = **0.025 dm^3**

Find the moles of EDTA that was used to react with the copper

Number of moles = volume x concentration

Trial 1: 0.02485 x 0.100 = **0.002485 mol**

Trial 2: 0.02490 x 0.100 = **0.002490 mol**

Find the moles of copper in the copper(II)sulphate

Trial 1 : 0.002485 mol
Trial 2 : 0.002490 mol
} same as EDTA due to molar ratio of 1:1

Calculate the concentration of the copper(II)sulphate solution

$$\text{Concentration (mol dm}^{-3}\text{)} = \frac{\text{number of moles}}{\text{Volume (dm}^3\text{)}}$$

Trial 1 using fast sulphon Black

Concentration = $\frac{0.002485}{0.025}$ (volume of titrant in dm^3)
= 0.0994
x
6
= **0.5964 mol dm^{-3}**

Trial 2 using murexide

Concentration = $\frac{0.002490}{0.025}$
= 0.0996
x
6
= **0.5976 mol dm^{-3}**

Note : → this is the factor by which to multiply back up to obtain the actual concentration.

There is also an alternative calculation method which can determine the concentration using the equation:

$$\mathbf{CA\ VA = CB\ VB}$$

Where:

CA = concentration of chemical A
VA = volume of chemical A
CB = concentration of chemical B
VB = volume of chemical B

Trial 1 using Fast sulphon Black

CA VA = CB VB

$= \mathbf{CA = \frac{CB\ VB}{VA}}$

Concentration = $\frac{0.100 \times 24.85}{25.0}$ (volume of the titrant in cm^3)

$= 0.0994 \times 6$ (diluting factor)

$= \mathbf{0.5964\ mol\ dm^{-3}}$

Trial 2 using murexide

CA VA = CB VB

$= \mathbf{CA = \frac{CB\ VB}{VA}}$

Concentration = $\frac{0.100 \times 24.90}{25.0}$

$= 0.0996 \times 6$

$= \mathbf{0.5976\ mol\ dm^{-3}}$

Conclusions

The calculations show that for the titration using the fast sulphon black indicator the concentration of the unknown copper solution is 0.5964 mol dm^{-3} and for the titration using the murexide indicator the concentration is 0.5976 mol dm^{-3}. The actual concentration of the unknown solution stands to be 0.60 mol dm^{-3} and therefore the titration using the murexide is more accurate than the fast sulphon black indicator titration, as the concentration value is closer to it.
The aim of this investigation was to determine which analytical technique is most accurate, precise and gives rise to reproducible results. These are the three critical aspects of this analytical technique which must be considered.

Trial 2 is a **replication** of trial 1 in terms of methodology. The difference, in terms of the concentration value, between the two trials is 0.0012 mol dm^{-3} which is very small (12/10 000) since the difference occurs in the fourth significant figure, and so can be considered negligible considering the limited nature of this investigation and the limitations due to the apparatus available, where the burette and balance can only enable readings to two decimal places. Taking these figures and factors into account, the conclusion on reproducibility stands to be that the methodology provides highly reproducible findings.

Precision is an aspect which confirms the effectiveness of the methodology used by looking at how small the difference is between the titres, and also confirms how accurate the results are. E.g.:

Trial 1 – fast sulphon black indicator

Final – Initial (cm^3)	**24.90**	**24.80**	**24.90**	**24.80**	**24.70**	**25.00**

Trial 2 – murexide indicator

Final – Initial (cm^3)	**24.80**	**24.90**	**25.00**	**25.00**	**24.90**	**24.80**

In trial 1, the titres agree to within 0.10, 0.20 and 0.30 cm^3. In trial 2, the titres agree to within 0.10 and 0.20cm^3. This indicates that in individual trials, the results are fairly precise; however comparing the two, trial 2 shows higher precision and accuracy as there is less variation between the titres. The difference between the average titres of trials 1and 2 is **0.05 cm^3**. This is lower than the accepted 0.10 cm^3 and so they conform to quite precise results. One major factor regarding the end-point is its detection. The titre value depends entirely on this and it is a subjective measurement. This means a strong conclusion about the extent of precision this technique offers cannot be made, as there is not ample external evidence to make comparisons with.

The only difference between the two trials is the indicator used, and this factor affects the **accuracy** of the analysis in terms of spotting the end-point. The Fast Sulphon indicator did not show a distinct end-point whereas the murexide trial showed a series of colours which are easier to spot. The spotting of the end-point is a subjective measurement however, as stated before, a distinct and spontaneous colour change was not obtained. Therefore the murexide trial is likely to be more accurate as the volume and concentration values lie closer to the true values of the "unknown" concentration compared to that of the Fast Sulphon black trial.
The conclusion on accuracy is that this analysis calculation on the difference between the concentration values shows a significant level of accuracy when using the murexide indicator, however since the apparatus only allows us to go to two decimal places, this would mean that the values were indeed the same. Referring to the evaluation, the percentage error between the actual concentration of the "unknown" and the experimentally determined values calculates to **0.00096%** which is extremely lower than the accepted 1% of error. The difference between the actual concentration and the murexide trail is 0.0024 mol dm^{-3} and this is a very small difference as it occurs in the thousandth column, and taking into account the limitations of the apparatus available, it is quite an accurate value.

There are reasons explaining why the experimental concentration values do not reflect the actual concentration value. One reason to consider is the transferring and washings. These processes require careful handling and sufficient washings. Since time was a constraint in this investigation, and because there are many techniques which have to be employed, the washings may not have removed all the copper(II)sulphate from the 250 dm^3 volumetric flasks and some spilling may have occurred which reduces the volume. Reductions in volume affect the concentration and since solutions of 1 litre have to be made, making up to the mark with distilled water further dilutes the solution. If there was more time, then several washings could have been made and the transferring could have been slower as to reduce spilling.

As stated before, a major reason for deviations between titres is the accurate determination of end-points. The Fast Sulphon indicator made the end-point hard to distinguish from the near end-point, and so the reading was actually lower than the theoretical 25 cm^3. Similarly, for the murexide trial, the end-point was difficult to pin point but it was relatively easy compared to the Fast Sulphon. If it was possible to use apparatus which allowed more than two decimal places in the measurements then this would further distinguish between which indicator used gave rise to a more accurate result.

Redox Titration analysis

Titration is a branch of quantitative chemistry, which enables us to determine the concentration of unknown substances (analyte) by adding a sample of known concentration (titrant) until the reaction is complete by the indication of a colour change. In this case the titration of copper iodide against sodium thiosulphate. Cu^{2+} ions react with excess iodide ions (I^-) forming a precipitate of copper(I) iodide and molecular iodine. The end-point is detected using an indicator in this case starch. Calculations can then be made using measurements of dispensed reagent volume to determine the unknown concentration of the analyte
Redox titrations involve the transfer of electrons. Redox equations can be split into two half equations: one showing acceptance of electrons; one showing the donation.
An oxidising agent is a substance that removes electrons from something else and a reducing agent gives electrons to something else. Oxidation and reduction can be worked out by looking at the ions involved in the equations.

$$2Cu^{2+}_{(aq)} + 4I^-_{(aq)} \longrightarrow Cu_2I_{2(s)} + I_{2(aq)} \quad (1)$$

Reduction = $2Cu^{2+} + 4e^- \longrightarrow 2Cu$

Oxidation = $4I^- \longrightarrow 2I_2 + 4e^-$

$$I_{2(aq)} + 2S_2O_3^{2-}{}_{(aq)} \longrightarrow 2I^-_{(aq)} + S_4O_6^{2-}{}_{(aq)} \quad (2)$$

Reduction = $2I_2 + 4e^- \longrightarrow 4I^-$

Oxidation = $2S_2O_3^{2-} \longrightarrow$

The equation in (1) shows that as the potassium iodide is added to the copper solution, a precipitate of copper(I)iodide is formed. The oxidation state of the copper ions decreases from +2 to 0; oxidation state of the iodide ions increases from -1 to 0.
Equation 2 shows that as the liberated iodine is titrated against the sodium thiosulpahate, the oxidation state of the molecular iodine decreases from 0 to -1; the oxidation state of the thiosulphate ion increases from -2 to _____
There are three equations useful for when working with concentrations:

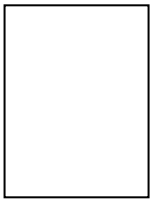
$C = \frac{n}{V}$ $\quad n = Cv \quad$ $v = \frac{n}{c}$

C = concentration (mol dm^{-3}); n = number of moles; v = volume (dm^3)

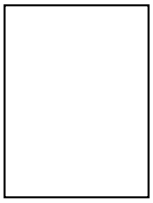
Advantages of titration

- Well-known quantitative technique, which gives rise to very accurate and precise results
- Fast, complete and observable end-point with a high degree of automation
- Relatively easy to set up and follow through.

Risk Assessment



Eye protection



wear gloves

Sodium thiosulphate : **HARMFUL**[27]

If ingested: may cause vomiting and cyanosis. Rinse mouth with plenty of water, and consume copious amounts of water. Seek medical attention immediately.
If spilt on skin: wash off with plenty of water
If splashed in eyes: rinse immediately with plenty of water, under the eyelids for at least 15 minutes.

Disposal: in accordance with the law.

Potassium iodide : **HARMFUL**[28]

If ingested: induce vomiting immediately. Seek medical attention.
If spilt on skin: wash affected area with water for at least 15 minutes and remove any contaminated clothing. Seek medical attention if irritation persists.
If splashed in eyes: immediately wash eyes under running water occasionally lifting upper and lower lids.

Disposal: dispose of in containers and make sure the containers are dealt with in waste management.

Ethanoic acid : **CORROSIVE**[29]

AVOID ALL CONTACT. If the chemical reaches the eyes then a burning sensation prevails followed by loss of vision.

If spilt in eyes or lab: remove contaminated clothing. Rinse skin and wash eyes with copious amounts of water and soap. Have a shower. Seek medical attention if irritation is experienced.
If ingested: ethanoic acid causes a burning sensation down the alimentary canal

[27] www.wm-blythe.co.uk

[28] www.jtbaker.com
[29] www.chem.ox.ac.uk

and results in diarrhoea. Rinse mouth with plenty of water and consume copious amounts of water. Avoid inducing vomiting and seek medical advice.

Disposal: neutralise the solution under careful supervision and dispose down sink. The solution to be prepared is very dilute (0.1 M) so not much hazard to be expected, however it is important to anticipate the unexpected.

Sodium carbonate: **HARMFUL**[30]

May cause eye burns and is harmful if swallowed, causes irritation to skin and respiratory tract.

If spilt on skin or lab: flush skin with plenty of water and soap. Remove any contaminated clothing and seek medical advice.
If ingested: avoid inducing vomiting, but swallow large amounts of water. Seek medical attention if irritation persists.

Disposal: dispose according to the law.

Preparations of the solutions

Sodium thiosulphate[31]

CALCULATIONS: 1 mol dm^{-3} solution = **248g**
So 0.1 mol dm^{-3} = 248/10 = **24.80g**

In titration methods all the solutions must have a molarity of 0.1 mol dm^{-3}.

I. Using a beaker, weigh out accurately 24.80g of the salt.
II. Add distilled water until the solid dissolves.
III. Transfer the solution and all subsequent washings to a 1dm^3 volumetric flask and make up to the line using distilled water.
IV. Mix the solution well by inverting the flask 20 times, and between each rotate the flask.
V. Transfer to a bottle and label 0.1 mol dm^{-3} sodium thiosulphate.

Sodium Carbonate

CALCULATIONS: M_r of Na_2CO_3 is 106.
1 mol dm^{-3} = 106g of Na_2CO_3
So 0.1 mol dm^{-3} = 106/10 = **10.6g**

[30] www.chinatrona.com
[31] Titrimetric Analysis for A and S Levels- JG Stark – ISBN: 0-7195-2446-6

VI. Heat the sodium carbonate at about 270 C for 45 – 60 minutes, on a clean nickel crucible, on a sand bath.
This is approximately 99.9% pure, and the heating removes final traces of moisture. It is necessary for the procedure to be carried out in the crucible.
VII. Allow to cool in desiccators for a bout half an hour. Stir the contents well with a clean nickel crucible.
VIII. Weigh out accurately about 1.6g of the dry anhydrous sodium carbonate, sealing the weighing bottle during the process to prevent any access of water vapour.
IX. Dissolve in minimum water and transfer to a 250cm^3 flask along with any washings. Make up to the line.
X. Label this 0.1mol dm^{-3} of sodium carbonate

Ethanoic acid

Since a dilute solution is needed, a 0.1 molar solution will need to be prepared

CALCULATIONS: M_r of ethanoic acid = 60.
1 mol dm^{-3} = 60g
So 0.1 mol dm^{-3} = 60/10 = **6.0g**

IV. Dissolve 6.0g of glacial ethanoic acid in water.
V. Transfer the solution to a 250 cm^3 flask along with any washings and make up to the line using distilled water.
VI. Label this 0.1 mol dm^{-3} of ethanoic acid (dilute)

Starch solution indicator[32]

I. Accurately measure out 10g of the starch into a weighing boat.
II. Transfer this to a beaker and add about 25cm^3 water to make a paste.
III. Set up a Bunsen burner and tripod and place a beaker with 800cm^3 of water. Bring to the boil.
IV. Transfer the paste to the beaker of boiling water and allow boiling again.
V. A thick light blue tinted solution should be the result.
VI. Allow to cool at room temperature and transfer to a bottle and label this 1% starch indicator.

The Redox titration method

I. Obtain a clean and dry beaker and pour some unknown concentration copper(II)sulphate solution.
II. Obtain two more beakers and pour some sodium carbonate solution into one and pour some ethanoic acid into the other. Label the beakers to avoid any confusion with the colourless solutions.

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III. Obtain another beaker and pour some of the starch indicator. Label this beaker.

IV. Set up a clamp and stand. Obtain a clean burette and rinse with distilled water, followed by the sodium thiosulphate solution.

V. With a funnel, fill the burette with sodium thiosulphate, making sure the bottom of the meniscus rests on the line.

VI. With a clean dropping pipette withdraw some sodium carbonate and pour into the unknown copper(II) sulphate solution until a faint blue precipitate is formed. This is a precipitate of copper(II) carbonate.

VII. With another clean dropping pipette, withdraw some Ethanoic acid and pour into the precipitated copper solution until the precipitate dissolves, and a clear solution is obtained.
This removes any traces of free mineral acid.

VIII. With a clean 25cm^3 volumetric pipette, withdraw 25cm^3 of the copper solution and transfer to a conical flask.

IX. Weigh out 1.5g of potassium iodide and transfer this to the conical flask. Notice the colour change: the solution becomes brown due to the formation of the copper(I) iodide precipitate and free iodine in solution.

X. With another clean dropping pipette, withdraw some starch solution and add three drops to the conical flask.
Notice the change: the solution still remains brown with some flecks of a navy-black substance. This is the starch iodine complex.

XI. Start the titration about 7 cm^3 at a time, continuously swirling the conical flask.

XII. Upon reaching the near end-point, the solution turns a peach colour with some of the flecks remaining. Reduce the flow of the burette to drop-wise.

XIII. Continue swirling the flask until all the iodine-starch complex has disappeared leaving behind a solution containing a white precipitate. This is the end-point.

XIV. This is the rough titre, note down the end-point.
Repeat steps **VIII** – **XIII** until all six titres are obtained.
When swirling the flask, take care not to spill or splash any solution as it is hazardous and alters the results.

For each titre, wash out the flask with distilled water thoroughly. This reduces the chances of contamination leading inaccurate and unreliable results.

Modifications to the method

Titrations involve the analysis of solutions with small molarities. The previous complexiometric titration method deduced that the approximate concentration of the unknown solution is 0.60 mol dm^{-3} and so the solution was diluted down to 0.10 mol dm^{-3}, using the same procedure as for the complexiometric titration (see complex titration method).

Implementation

Results Table for Redox Titration analysis

Trial 1

	Test						
	Rough	**T1**	**T2**	**T3**	**T4**	**T5**	**T6**
Initial Burette reading (cm^3)	0	0	0	0	0	0	0
Final Burette reading (cm^3)	25.00	25.50	25.30	25.70	25.20	25.30	25.60
Final – Initial (cm^3)	**25.00**	**25.50**	**25.30**	**25.70**	**25.20**	**25.30**	**25.60**

Average Titre = $\frac{\text{6 titres}}{6}$ = $\frac{25.50+25.30+25.70+25.20+25.30+25.60}{6}$ = $\frac{152.60}{6}$

= **25.40**

Trial 2

	Test						
	Rough	**T1**	**T2**	**T3**	**T4**	**T5**	**T6**
Initial Burette reading (cm^3)	0	0	0	0	0	0	0
Final Burette reading (cm^3)	25.00	25.40	25.40	25.50	25.30	25.30	25.60
Final – Initial (cm^3)	**25.00**	**25.50**	**25.30**	**25.70**	**25.20**	**25.30**	**25.60**

Average Titre = $\frac{\text{6 titres}}{6}$ = $\frac{25.50+25.30+25.70+25.20+25.30+25.60}{6}$ = $\frac{152.60}{6}$

= **25.40**

Analysis of results

Since the copper sulphate solution of "unknown" concentration was diluted from 0.60 to 0.10 mol dm^{-3}, and the molarity of the sodium thiosulphate solution was made to 0.1 mol dm^{-3}, in theory, the balanced chemical equation shows that **equal volumes** react completely with each other. If 25.0 cm^3 of the copper(II)sulphate solution was pipetted into the conical flask then **25.0 cm^3** of the sodium thiosulphate solution should, in theory, react completely with the excess iodine. Using the equations below, we can work out the concentration of the copper (II) sulphate solution.

1 mol $Cu^{2+}_{(aq)}$ = **1** mol $S_4O_6^{2-}{}_{(aq)}$

The equation shows that the stoichiometric ratio is 1:1, so 1 mole of the copper ions react with 1 mole of the thiosulphate ions.

First all the volumes used must be converted to dm^3

$$\frac{X}{1000}$$

X ← the volume (cm^3)

1000 ← the conversion of cm^3 to dm^3

Average titre of	
Trial 1	**Trial 2**
$\frac{25.40}{1000}$	$\frac{25.40}{1000}$
0.02540 dm^{-3}	**0.02540 dm^{-3}**

Find the moles of thiosulphate that was used to react with the copper

Number of moles = volume x concentration

Trial 1: 0.02540 x 0.100 = **0.002540 mol**

Trial 2: 0.02540 x 0.100 = **0.002540 mol**

Find the moles of copper in the copper(II)sulphate

Trial 1 : 0.002485 mol
Trial 2 : 0.002490 mol
} same as thiosulphate ions due to molar ratio of 1:1

Calculate the concentration of the copper(II)sulphate solution

$$\text{Concentration (mol dm}^{-3}\text{)} = \frac{\text{number of moles}}{\text{Volume (dm}^3\text{)}}$$

Trial 1

$$\text{Concentration} = \frac{0.002540}{0.025 \text{ (volume of titrant in dm}^3\text{)}} = 0.1016 \times 6 \text{ (dilution factor)}$$

$$= \mathbf{0.6096 \text{ mol dm}^{-3}}$$

Trial 2

$$\text{Concentration} = \frac{0.002540}{0.025} = 0.1016 \times 6$$

$$= \mathbf{0.6096 \text{ mol dm}^{-3}}$$

Note : → this is the factor by which to multiply back up to obtain the actual concentration.

There is also an alternative calculation method which can determine the concentration using the equation:

$$\mathbf{CA\ VA = CB\ VB}$$

Where:

CA = concentration of chemical A
VA = volume of chemical A
CB = concentration of chemical B
VB = volume of chemical B

Trial 1

CA VA = CB VB

$= \mathbf{CA = \frac{CB\ VB}{VA}}$

$= \frac{0.100 \times 25.40}{25.0}$ (volume of the titrant in cm^3)

= 0.1016
x
6 (dilution factor)

= **0.6096 mol dm^{-3}**

Trial 2

CA VA = CB VB

$= \mathbf{CA = \frac{CB\ VB}{VA}}$

$= \frac{0.100 \times 25.40}{25.0}$

= 0.1016
x
6

= **0.6096 mol dm^{-3}**

Conclusions

Both forms of the calculations for both the trials show that the experimentally determined concentration for the "unknown" solution is **0.6096 mol dm^{-3}**. The actual concentration for the "unknown" solution stands to be 0.60 mol dm^{-3}.
The aim of this investigation was to determine which analytical technique is most accurate, precise and gives rise to reproducible results. These are the three critical aspects of this analytical technique which must be considered.

Trial 2 is a **replication** of trial 1 in terms of the methodology. The procedure was followed as planned and the results produced were exact replicas of each other at 0.6096 mol dm^{-3}. The two average titres are slightly higher than the concentration of the "unknown" copper sulphate solution by **0.0096** mol dm^{-3}, and to two decimal places, it is **0.01 mol dm^{-3}**. This difference can be considered negligible as it occurs in the thousandth figure bearing in mind the limitations of the experiment in terms of the apparatus available and the tentative nature of the line of enquiry. In conclusion on this aspect, the methodology allows for the technique to give rise to highly replicable results.

When results are concordant to each other by a certain degree, we say they are precise. **Precision**, when it concerns titrations, is confirmed by looking at how small the difference is between the titres. E.g.:

Trial 1

Final – Initial (cm^3)	**25.50**	**25.30**	**25.20**	**25.70**	**25.30**	**25.60**

Trial 2

Final – Initial (cm^3)	**25.50**	**25.70**	**25.30**	**25.60**	**25.20**	**25.30**

In both trials 1 and 2, the titres agree to within 0.10, 0.20, 0.30 and 0.50 cm^3. This indicates that the titres are not quite precise, as the standard variation is 0.10 cm^3 and the titres exceed this limit. In short, the technique does not give rise to highly precise results; however there is a factor to consider regarding the subjective nature of spotting the end-point, as the titre value depends entirely on spotting the end-point. As stated in the complexiometric titration method, a strong conclusion cannot be made due to the tentative nature of this investigation.

The **accuracy** of the technique can be considered by determining the percentage error between the actual concentration of the "unknown" solution and the

experimentally determined value. From the evaluation, the error calculates to **0.96%**, which is lower than the accepted 1% of error. This means the technique has a high value of accuracy, even though the experimentally determined value is higher than the actual concentration of the "unknown" solution. This extra 0.0096 mol dm^{-3} could be due to the experimental nature of this experiment. The conclusion on this aspect is that this analysis shows a significant level of accuracy, taking into account the very small difference between the experimentally determined concentration and the actual "unknown" concentration as it occurs in the ten thousandth column and taking into account the apparatus available, it is quite an accurate value.

There are reasons explaining why the experimental concentration values do not reflect the actual concentration value. One reason to consider is the transferring and washings. These processes require careful handling and sufficient washings. Since time was a constraint in this investigation, and because there are many techniques which have to be employed, the washings may not have removed all the copper(II)sulphate from the 250 dm^3 volumetric flasks and some spilling may have occurred which reduces the volume. Reductions in the volume of the solution affect the concentration and since solutions of 1 litre have to be made, making up to the mark with distilled water further dilutes the solution. If there was more time, then several washings could have been made and the transferring could have been slower as to reduce spilling.

The main limitation of this investigation is the precision of the technique. The difference between the titres for both the trials is too great and exceeds the accepted 0.10 cm^3. The end-point was relatively easy to spot, compared to the complexiometric titration, however there could have been mistakes in judging whether all the iodine-starch complex had been removed. Since the flask needed swirling, sometimes it appeared as if the iodine-starch complex had been removed when in fact it hadn't when the flask was stationery. This complication made it hard for the accurate determination of the end-point and could have accounted for the slight overestimation of the burette reading.

Gravimetric Analysis

Determining the quantitative amount of a substance by the processes of precipitation, isolation and finally subsequent weighing of the precipitate is called **gravimetric analysis**. This analysis, in the most basic situation, could simply entail heating a sample to its anhydrous state and weighing it to determine the amount of volatile constituents. The other type of gravimetric analysis is that which involves determining the amount of a particular substance in an aqueous media by means of precipitation reactions. The precipitation reactions give a more accurate measure of the amount of substance therefore I have chosen this method.

Gravimetric analysis is fairly straightforward. A weighed amount of the substance to be analyzed is dissolved and a more reactive metal is added in slight excess to displace the copper. After this a process called **nucleation** occurs, where the nuclei of atoms accumulate and form "lumps" of atoms. It is from these that the crystals will grow. This then leads to the **particle growth** period where large nuclei grow at the cost of smaller nuclei, since it gives rise to larger crystals. The growth of larger crystals can be provoked by a process called **digestion** where the precipitate is heated with the 'mother liquor'[33] for some time. Digestion is an important part of the process as reduces the surface area of the solid and propagates a more ordered arrangement within the crystallites. The advantage of this is that it reduces surface adsorption and chances of occlusion of impurities. This precipitate is then filtered, dried and weighed. The latter two procedures repeated over and over. From the mass of the precipitate and the known composition, the amount of the wanted substance can be worked out.

In this investigation, the unknown concentration of copper(II) ions in its sulphate salt is to be determined by adding excess zinc dust .Copper ions form a blue colour in solution and adding zinc displaces the copper making the solution colourless. The concentration of copper is related to the colour of the solution and if any cations remain, the solution is still blue, but very pale.

The reaction is an exothermic redox reaction where the copper ions are reduced to copper metal and the zinc metal particles are oxidised to zinc ions in a sulphate medium. The suspension still contains unreacted zinc and so concentrated sulphuric acid (4 M) is added to remove the zinc.
The proper procedure of drying and heating and weighing the copper precipitate involves carrying it out in an inert atmosphere such as argon as this prevents the copper from being oxidised. Copper is oxidised in high temperatures and this adds to the weight of the precipitate. In such occasions, the copper can undergo a reduction process by passing methane gas over it.

$$8CuO + 2CH_4 \longrightarrow 8Cu + 2CO_2 + 4H_2O$$

[33] http://www.newi.ac.uk/buckly/gravi.htm

Some inorganic precipitates [34]

Reagent	Analyte and form precipitated	Analyte form weighed
$NH_{3(aq)}$	Be hydrous oxide	BeO
	Al hydrous oxide	Al_2O_3
$AgNO_3$	AgCl	AgCl
	AgBr	AgBr
	AgI	AgI
$BaCL_2$	$BaSO_4$	$BaSO_4$

For accurate determinations, the precipitate must meet the following criteria:

I. The wanted substance must precipitate out completely. In many sample determinations the precipitate has a low value such that 'quantitative separations can be made'[35]We must also consider the 'common ion' effect further reduces the solubility of the precipitate. Take the example of copper sulphate$_{(aq)}$ into copper$_{(s)}$. Adding an excess of the 'zinc dust' would mean more copper ions can be precipitated out of solution as equilibrium is shifted to the right.
II. 'The stoichiometric composition of the dried and weighed state of the product must be known so the weight can be related to the amount of analyte present'[36].
III. The product should have a primary standard, because this produces a sample which is 99.9% pure, and must be readily filterable. Obtaining a pure product is difficult as impurities are inevitably present. However careful and sufficient washing with sulphuric acid & water assists in keeping the level of impurity to a minimum for all gravimetric analysis.
IV. Precipitation from hot solutions. Increasing temperature increases the solubility of precipitates and hence decreases the super saturation. This procedure also reduces the chances of surface adsorption of unwanted materials.
V. Washing and filtering using hot electrolyte reduces the hassles associated with co precipitation and adsorption.

[34] principles and practices of analytical chemistry- F.W. Fifield and D Kealey- 1983
[35] principles and practices of analytical chemistry- F.W. Fifield and D Kealey- 1983
[36] principles and practices of analytical chemistry- F.W. Fifield and D Kealey- 1983

VI. A biochemical process called peptization prevails during washings and involves part of the precipitate to revert to the colloidal state e.g.:

$$\text{Ag Cl(colloidal)} \longrightarrow \text{Ag Cl (s)}$$ [37]

This change means part of the precipitate is lost through filtration. This can be reduced by washing with hot electrolyte. Precipitates formed from colloidal agglomeration have amorphous structures with a large surface area. To improve this, the precipitation procedure should be done whilst heating.

The above information was considered in deciding the reasons for selecting zinc powder as the precipitating agent, as the stoichiometric ratio of copper : sulphate and zinc : sulphate is 1:1 so any calculations to be made are easy to work with. Also zinc sulphate has a higher solubility constant than the copper sulphate so it does not precipitate out along with the copper. To reduce impurities and co-precipitation, the method to be used will involve heating the copper(II)sulphate solution whilst the zinc is added.

Gravimetric analysis has a wide range of applications such as 'routine assays of metallurgical and mineralogical samples'.[38] The analysis of rocks, soil and such depend highly on gravimetric analysis due to the relative accuracy of weighing quantities of really low masses (0.1-0.00001g).

Disadvantages

The method has some drawbacks in terms of the practicalities. The method requires careful precision and a steady hand is needed in making the weighing. The apparatus used also needs to be scrupulously clean and the method as a whole is very time-consuming due to the drying and weighing processes.

Apparatus

- Glass rod
- 500cm^3 Glass beaker
- 1dm^3 volumetric flask
- glass measuring cylinder 100cm^3
- access to an ice bath and fume cupboard
- access to an analytical balance (4+ sig.fig.)
- access to an oven
- fine-grade filter paper
- Buchner funnel and flask

[37] http://www.newi.ac.uk/buckly/gravi.htm
[38] principles and practices of analytical chemistry- F.W. Fifield and D Kealey- 1983

Materials

- 135cm^3 of sulphuric acid
- unknown concentration of copper(II) sulphate solution
- zinc metal powder
- distilled water

Justification of apparatus

The ice bath is used for the preparation of sulphuric acid as mixing it with water is an exothermic reaction, the ice will absorb the heat.

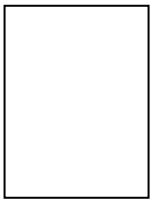
Sulphuric acid is very corrosive to the skin therefore a fume cupboard must be employed when carrying out measurements and transferrings.

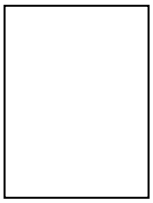
The filter paper has to be of fine-grade in order to retain the maximum amount of precipitate possible.

The Buchner funnel is the specialised piece of eqipment used to carry out immediate filtration. This apparatus enables rapid filtration compared to the conventional filter funnel.

The oven is used to dry the precipitate and is used instead of a dessicator because it is quicker to dry things. The oven must have heat settings upto 120C as the temperature needed varies with different compounds.
The balance must give readings with significant figures of upto 4 and more. This enables more accurate values to be determined.

Risk Assessment


Eye protection


Wear gloves

Sulphuric acid: **CORROSIVE** [39]

WARNING: addition of acid to water is a highly exothermic reaction. Never add water to acid, always acid to water. Take care when pouring and stirring,

[39] hazcards

Use only glassware when preparing the solution, as any plastic apparatus may be corroded by the strong acid.

If ingested: rinse out the mouth and give two glasses of water folowed by 'milk of magnesia'. Then seek medical attention.
If splashed in eyes: rinse eyes with gently running water, then seek medical advice.
If spilt in lab: ventilate the area well. Lay down mineral absorbent and scoop up into a container. Rinse the area well with water and soap.

Disposal: dispose of according to the law.

Copper(II) sulphate : **HARMFUL**

No appreciable hazard

If ingested: rinse mouth with water, and then consume a copious amount. If irritation
persists then seek medical attention.
If splashed in eyes: rinse eyes gently with running tap water. If irritation persists seek medical attention.
If spilt: no appreciable hazard to clothes. If spilt in laboratory then make sure the area washed with water and cleaned up.

Disposal: down sink with copious amounts of water, as copper is a toxic metal to plants and inhibits growth, therefore harming the environment.

Preparation of the solutions[40]

Sulphuric acid

I. Place at least 2 thirds of the final volume of water into a 500cm^3 beaker. For 365cm^3 of total volume of water, 2 thirds = 200cm^3 of water.
II. Measure out 135cm^3 of the acid using a clean glass measuring cylinder. Make sure this procedure is carried out in a fume cupboard.
III. Slowly pour the acid, into the beaker containing the water, in a thin stream while stirring with the glass rod, transferring all washings.
Note: this must be done in an ice bath, as the reaction is highly exothermic when cool.
IV. Make up the rest of the volume with distilled water and transfer to a 500cm^3 volumetric flask.
V. Stopper the flask and label it 5M sulphuric acid and corrosive label.

[40] recipe cards

The gravimetric method

I. The analytical balance must be calibrated to ensure the balance is flat on the work surface. This is done by adjusting the two dials on either side of the balance which adjusts the leg heights. The bubble of air must be within the circle.
II. Determine the weight of 20 fine-grade filter papers and then average them to find an accurate weight value.
III. Obtain a clean beaker and pipette 100cm^3 of the unknown concentration copper(II) sulphate into it.
IV. Add zinc dust, in small amounts, to the beaker with gentle stirring. Keep adding the zinc dust until the solution is no longer the characteristic blue colour and all the copper has been displaced. Allow the suspension to settle in order to see the colour.
V. Add 4 mol dm^{-3} sulphuric acid to the beaker, because it contains unreacted zinc metal, until there is no further effervescence i.e. no more bubbling. Leave overnight.
VI. Set up a Buchner funnel and place a filter paper in the funnel. Dampen it with distilled water.
VII. Pour the contents of the beaker into the funnel and washings and allow the vacuum filtration to commence.
VIII. Wash the copper twice with 10cm^3 of distilled water, and the same with the propane. On each occasion, turn off the vacuum to give the liquid time to soak into the copper.
IX. Allow air to be sucked through the copper to carry away any propanone as vapour. Then spread out the copper in a weighed filter paper.
X. Place filter paper in a dessicator and leave overnight. This ensures the precipitate is thoroughly dried.
XI. Place the filter paper in an oven and preheat to 65 C. Dry for at least 20 minutes.
XII. Cool the precipitate and filter paper to room temperature and place in the gravimetric balance and determine the weight. Record the mass of the filter paper + precipitate.
XIII. Heat again for 15 minutes, cool a then weigh.
XIV. Repeat procedure XII and XIII until three constant weight value are obtained.

Modifications to the method

The temperature of the oven was initially set at 100 C. since the filter paper has to be placed in the oven; there is a problem of it absorbing or losing moisture. A filter paper was weighed before and after it was heated in the oven at 100 C for 5 minutes and the weight dropped from 0.2434 to 0.2402, which means it lost moisture. So the temperature was lowered to 60 – 70 C which is enough for efficient drying.

Preliminaries showed that 100 cm^3 of the unknown copper(II)sulphate of approximate concentration of 0.60 mol dm^{-3} would yield 3.76 g of copper. The calculations are as follows:

<u>100 cm^3 of Copper(II)sulphate:</u>

Number of moles = C x V
= 0.6 x 0.1
= **0.06 mol**

Mass = n x M_r
= 0.06 x 249.5
= **14.97 g of copper(II)sulphate**

<u>% of copper in copper(II)sulphate:</u>

$$\frac{14.97}{63.5} \times 100$$

= **23.5%**

<u>Theoretical yield of elemental copper</u>

= 0.235 x 14.97
= **3.6895 g of copper**

This is more than enough copper to weigh and dry.
The suspension of zinc dust and precipitated copper in sulphuric acid has to be left over-night to ensure the excess zinc completely reacts with the sulphuric acid.

When copper is dried, the characteristic dull bronze colour should appear which indicates the moisture is evaporating. When the first trial was conducted, the copper precipitate colour did not change, instead, the colour remained dark brown. In addition, upon reaching three constant weight values (see results table), these values did not reflect the theoretical yield of copper that should be obtained from the 100cm^3 of 0.60 mol dm^{-3} of copper(II)sulphate solution. These signs and values indicate that the unidentified cause of the remaining weight could be due to oxidation of the copper.
The second trial was done and the same trends were produced. This replication confirms that there was some oxidation which occurred. Due to this unexpected result, a reduction procedure was employed.

Reduction of the copper (II) oxide using methane gas

I. The apparatus must be set up behind a safety shield
II. Obtain a clean, dry test tube. Weigh and record the mass.
III. Add all the copper (II) oxide carefully with a metal scoop, so as little as possible of the powder gets on the side of the test tube.
IV. Set up a support stand and clamp the glass tube connected to the methane gas supply.
V. Place the test tube, attached to another support stand, under the mouth of the glass tube connected to the methane gas supply carefully so that it does not touch the powder. The glass tube should extend far into the test tube, but do not touch either the solid in the test tube or the tube itself.
VI. Light a match and turn on the source of methane gas for the glass tube inserted into the test tube.
VII. Light a Bunsen burner and adjust it to hottest flame. Move the burner under the sample. It may then be moved back and forth to provide even heating. The sample is black to brown before heating.
VIII. Heat the exterior of the test tube to a high temperature with the Bunsen burner for about 5 – 7 minutes, or until the characteristic copper colour appears in the material in the test tube.
IX. Turn off the Bunsen burner but keep the methane flowing through the inside of the test tube until the test tube cools down (about 5 minutes).
X. Cautiously test the temperature. (because of the heat released at the mouth of the tube when the methane is burning, the tube will not cool to room temperature. Once the gas is turned off, wait until the tube does cool to room temperature).
XI. Reweigh the test tube and copper. Record the mass. The weight of the copper can then be determined by subtracting the weight of the test tube from the weight of the tube+copper.

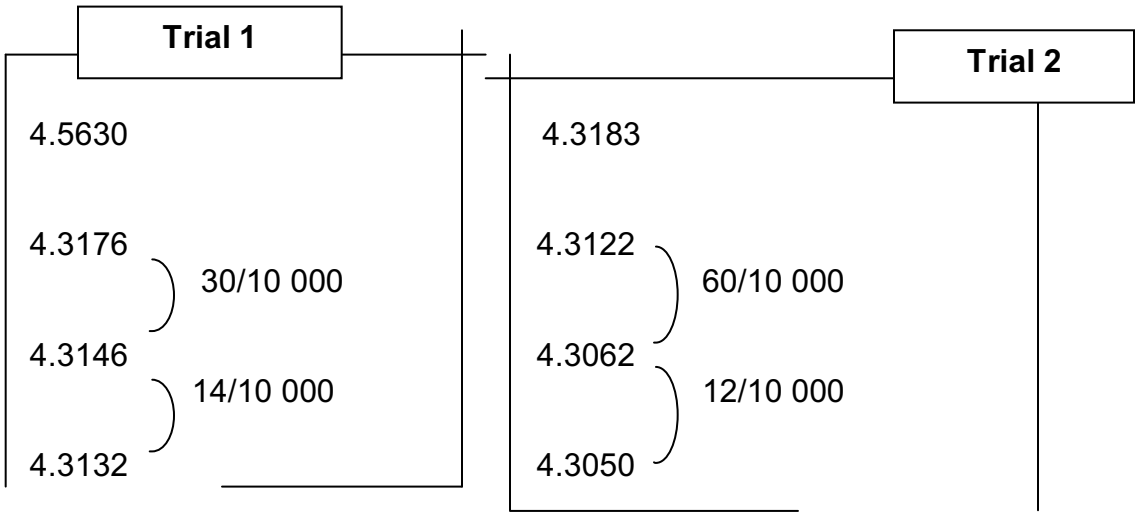
Implementation

Results table for Gravimetric analysis

Trial 1	No. of times dried and weighed						
	1	2	3	4	5	6	7
Weight of filter paper g (A)	← 0.2476 g →						
Weight of filter paper+precipitate g (B)	4.5630	4.3176	4.3146	4.3132			
Weight of precipitate g = (B-A)	4.3154	4.0700	4.0670	4.0656	4.0224		

Trial 2	No. of times dried and weighed						
	1	2	3	4	5	6	7
Weight of filter paper g (A)	← 0.2476 →						
Weight of filter paper+precipitate g (B)	4.3183	4.3122	4.3062	4.3050			
Weight of precipitate g = (B-A)	4.0707	4.0646	4.0592	4.0574	4.0306		

On both trials, only 4 drying and weighing procedures were sufficient because the last three values are constant, taking into account the limitation of not obtaining more accurate values from analytical balance available.



The above illustration shows that the last three weighings are indeed considered constant, taking into account the limitation of the available balance. In trial 1, the difference of weight occurs in the thousandth significant figure. Between the 2nd and 3rd weight values, the difference is 30/10 000 which is large but since it occurs in the thousandth sig. fig., it is relatively minute. Also, between the 3rd and 4th weight values, the difference is much smaller and so is considered concordant with the 3rd value. In trial 2, the difference between the 2nd and 3rd values is twice as large compared to trial 1, but considering it occurs in the thousandth sig. fig. it is still relatively minute. The same trend for the difference between the 3rd and 4th values occurred as in trial 1.

20 filter papers weighed:

0.2453+0.2423+0.2434+0.2510+0.2441+0.2434+0.2414+0.2404+0.2494+0.2528
+0.2496+0.2567+0.2500+0.2434+0.2534+0.2540+0.2456+0.2500+0.2518+
0.2158+0.2452 = 4.9524

$\frac{4.9524}{20}$ = **0.2476 g** is the average weight of the filter paper.

Results table for the Copper Reduction

Legend

The test tube used for the reduction could not contain all the precipitated copper and so the amount had to be halved and so 1.2 means the second half of trial 1.

Trial 1.1

Property	Weight (g)
Mass of ceramic paper	0.5100
Mass of test tube	30.2700
Mass of ceramic paper + test tube	30.7800
Mass of test tube + copper oxide	32.2200
Mass of test tube + copper	32.0500
Mass of copper oxide	1.9500
Mass of copper	1.7801
Mass of oxygen	0.1699

Trial 1.2

Property	Weight (g)
Mass of ceramic paper	0.5100
Mass of test tube	29.1000
Mass of ceramic paper + test tube	29.6100
Mass of test tube + copper oxide	30.2500
Mass of test tube + copper	29.2501
Mass of copper oxide	1.1000
Mass of copper	0.9499
Mass of oxygen	0.1501

Trial 1.3

Property	Weight (g)
Mass of ceramic paper	0.5000
Mass of test tube	29.4700
Mass of ceramic paper + test tube	29.9700
Mass of test tube + copper oxide	30.4900
Mass of test tube + copper	30.3700
Mass of copper oxide	1.0200
Mass of copper	0.9010
Mass of oxygen	0.1190

Trial 2.1

Property	Weight (g)
Mass of ceramic paper	0.5100
Mass of test tube	30.2700
Mass of ceramic paper + test tube	30.7800
Mass of test tube + copper oxide	32.2200
Mass of test tube + copper	31.9501
Mass of copper oxide	1.9500
Mass of copper	1.6801
Mass of oxygen	0.2699

Trial 2.2

Property	Weight (g)
Mass of ceramic paper	0.5100
Mass of test tube	29.1000
Mass of ceramic paper + test tube	29.6100
Mass of test tube + copper oxide	30.2000
Mass of test tube + copper	29.8488
Mass of copper oxide	1.1000
Mass of copper	0.7488
Mass of oxygen	0.3512

Trial 2.3

Property	Weight (g)
Mass of ceramic paper	0.5000
Mass of test tube	29.4700
Mass of ceramic paper + test tube	29.9700
Mass of test tube + copper oxide	30.0506
Mass of test tube + copper	29.8609
Mass of copper oxide	0.7806
Mass of copper	0.5909
Mass of oxygen	0.1897

Analysis of results

The decision to measure out 100 cm^3 of the unknown copper(II)sulphate solution to use in the precipitation reaction was based on calculations that showed it would theoretically yield 3.6895g of copper which is enough precipitate needed to carry out the drying and weighing procedures. Now that the weight values from both trials have been obtained, working backwards with the mole equations that were used to determine the theoretical yield, the molarity of the unknown concentration solution can be worked out using the mass values determined from the gravimetric method.

Summary of results for gravimetric balance weight values

	Weight (g)	
	Trial 1	Trial 2
	4.0224	4.0306

Find the concentration of the unknown solution from trial 1 results

Mass obtained : 4.0224
Number of moles of copper in this amount :

$$\text{Number of moles} = \frac{\text{Mass (g)}}{M_r}$$

$$\frac{4.0224}{63.5} = \mathbf{0.063\ mol}$$

Concentration of copper (II) sulphate :

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

$$= \frac{0.063}{0.1}$$

$$= \mathbf{0.63\ mol\ dm^{-3}}$$

Find the concentration of the unknown solution from trial 2 results

Mass obtained : 4.0306
Number of moles of copper in this amount :

$$\text{Number of moles} = \frac{\text{Mass (g)}}{M_r}$$

$$\frac{4.0306}{63.5} = \mathbf{0.063\ mol}$$

Concentration of copper (II) sulphate :

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

$$= \frac{0.063}{0.1}$$

$$= \mathbf{0.63\ mol\ dm^{-3}}$$

These results are similar with the colorimetric results with the exception of an additional 0.01 mol dm^{-3} and can be accepted. However, due to the possibility of oxidation of the copper, more calculations can be made from the results of the copper reduction process.
The difference between the theoretical yield and trial 1 copper weight is 0.3329, which calculates to $\frac{0.3329}{3.6895} \times 100 =$ **9%** of extra weight due to unidentified cause. The difference between the theoretical yield and trial 2 copper weight is 0.3411which calculates to $\frac{0.3411}{3.6895} \times 100 =$ **9.2%** of extra weight due to unidentified cause. This could be due to oxidation of copper, as in high temperatures this process occurs and the oven could have been the source of this temperature, and so the results from the copper reduction can be calculated to find the concentration of the unknown solution of copper(II) sulphate using the calculations as before.

Accumulating the weight values of the copper reduction

Since all the 3.6895g of copper precipitate could not fit into the test tube at once, the amount had to be divided into three parts. The calculations which follow are simply adding together the three weight values.

Trial 1

Property	Weight (g)
Mass of copper from 1.1 + 1.2 + 1.3	1.7801+ 0.9499 + 0.9010 = **3.6310**
Mass of oxygen from 1.1 + 1.2 + 1.3	0.1699 + 0.1501 + 0.1190 = **0.4390**

Trial 2

Property	Weight (g)
Mass of copper from 2.1 + 2.2 + 2.3	1.6801 + 0.7488 + 0.5909 = **3.0198**
Mass of oxygen from 2.1 +2.2 + 2.3	0.2699 + 0.3512 + 0.1897 = **0.8108**

Summary of results for copper reduction weight values

Weight (g)	
Trial 1	Trial 2
Copper = 3.6310 Oxygen = 0.4390	**Copper = 3.0198** Oxygen = 0.8108

Find the concentration of the unknown solution from trial 1 reduction results

Mass obtained : 3.6310
Number of moles of copper in this amount :

$$\text{Number of moles} = \frac{\text{Mass (g)}}{M_r}$$

$$\frac{3.6310}{63.5} = \mathbf{0.057\ mol}$$

Concentration of copper (II) sulphate :

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

$$= \frac{0.057}{0.1}$$

$$= \mathbf{0.57\ mol\ dm^{-3}}$$

Find the concentration of the unknown solution from trial 2 reduction results

Mass obtained : 3.0198
Number of moles of copper in this amount :

$$\text{Number of moles} = \frac{\text{Mass (g)}}{M_r}$$

$$\frac{3.0198}{63.5} = \mathbf{0.047\ mol}$$

Concentration of copper (II) sulphate :

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

$$= \frac{0.047}{0.1}$$

$$= \mathbf{0.47\ mol\ dm^{-3}}$$

Conclusions

There are two sections to this gravimetric analysis – the strict gravimetric weighing and then the extended copper reduction - which means there are two sets of results to analyse. The gravimetric analysis gave weight values of **4.0224g** for trial 1 and **4.0306g** for trial 2. The copper reduction reduced the weight values to **3.6310g** for the trial 1 copper and **3.0198g** for the trial 2 copper. The aim of this investigation was to determine which analytical technique is most accurate, precise and gives rise to reproducible results. These are the three critical aspects of this analytical technique which must be considered.

When we talk about the **reproducibility** of the results, it means that replications of the procedure as planned give rise to similar results each time. The extent of the reproducibility of this technique can be established by comparing the final concentration values of both trials, of both the initial gravimetric analysis and then the copper reduction process.
The results are as follows: for the gravimetric analysis, the weight of the copper for trial 1 was 4.0224 g and 4.0306 g for trial 2. The difference between these weight values is **0.0082 g**. This value is very minute and can be considered negligible as the analytical balance available does not allow any further accuracy. When these weight values were converted into concentrations, they were 0.63 mol dm^{-3} for both trials. Since this investigation focuses on the precision of the concentration values, it means that **so far** the analytical technique gives rise to precise results, as they are identical.
However, as mentioned previously (see introduction and analysis), the **copper** reduction was employed due to the possibility of the copper undergoing oxidation. This could have accounted for the much higher weight value than was calculated from the theoretical expectation. The copper reduction values obtained were: 3.6310 g after trial 1 and 3.0198 g after trial 2. The difference between these values is **0.6112 g**. This value may not appear to be quite large but when the weight values were converted to concentrations, they had a difference of 0.10 mol dm^{-3}.

The conclusion on this aspect stands to be that the technique after all does not ensure reliability. But there are several very important factors which account for the variation between the experimentally determined concentration values from the copper reduction and the actual concentration of the “unknown” solution of copper sulphate. These include occluded oxygen and zinc within the larger lumps of the copper and also the fact that not all the copper was transferred to the ceramic paper when carrying out the reduction with the methane gas. (See later).

The **precision** of the technique is determined by comparing the variance between the concentration values.

Initial gravimetric analysis

Trial 1 (mol dm^{-3})	**"unknown" concentration**	Trial 2 (mol dm^{-3})
0.63	0.60 mol dm^{-3}	**0.63**

From the initial gravimetric analysis the concentration values of trials 1and 2, there is no variance as they are both 0.63 mol dm^{-3}. So far we can assume that the technique allows for precise results to be obtained. However, after carrying out the reduction process, the concentration values greatly reduced, and also the variance between the two concentration values increased. The variance between the concentration values of trial 1 and trial 2 was 0.10 mol dm^{-3}, and this means there is a very large percentage difference error.

copper reduction analysis

Trial 1 (mol dm^{-3})	**"unknown" concentration**	Trial 2 (mol dm^{-3})
0.57	0.60 mol dm^{-3}	**0.47**

These figures indicate that the technique is very poor in terms of precision due to the variance however; to be critical, attention must be given to the factors -such as those mentioned earlier- which contributed to such a high variance (see later).

Finally, the **accuracy** of the technique can be considered. A result which relates by only 1% of error to the actual value constitutes to a very high degree of accuracy of the technique. From the evaluation it is calculated that there is a **0.15%** error between the trial concentration value and the "unknown" solution value, and **2.6%** error for trial 2. These values indicate that the trial 1 analysis conforms to a high degree of accuracy as the percentage is very small bearing in mind the limited experimental nature of this investigation. However; for the trial 2 analysis, the procedure does not conform to accuracy because the percentage difference error exceeds the accepted 1% error. The results from the trial 2 analysis do however need to be reconsidered in account of the factors also affecting the reliability and precision of this technique.

The precision, reliability and accuracy of this technique have all been affected by the following factors:

- **The remaining occluded oxygen and zinc**.

Firstly, the copper particles that were precipitated were quite big lumps. This means the lumps of copper particles still contained some oxygen and zinc trapped inside. One of the drawbacks of having a crude method is the fact that during the precipitation process, the unreacted zinc can be trapped in the precipitated lattice of the copper. This inevitably adds to the mass of the copper. Also, due to the highly exothermic nature of the displacement reaction of the copper sulphate solution and zinc powder means some oxidation will already have occurred.

Secondly, throughout the entire weighing and drying to constant weight process, the copper was of a fairly high temperature because the oven used was not very accurate at regulating the temperature and keeping it constantly at 65 C. The intervals where the copper was being weighed were very lengthy on the analytical balance as it is very sensitive and required time to reach a fixed weight value. These were perfect opportunities for oxidation to occur and also the colour of the copper changed, getting darker and darker after each drying process. This leaves us with the conclusion that this could have resulted in the higher than expected values determined from the initial gravimetric analysis.

- **Not all the copper was transferred onto the ceramic paper.**

It is inevitable that when transferring the solid from one container to another, some residues remain unless it is washed off and transferred. It was not possible to wash the copper off the filter paper and onto the ceramic paper and so some of it remained on the filter paper. Scraping the copper off the filter paper was not possible either because some of the paper could scrape off, and this would contaminate the copper as well as add to the weight. A spatula was used to carry out the transferring and inevitably some copper remained on the spatula.

From the above factors, we can conclude that there are many weak points to this crude procedure, where the handling of the copper is by far the factor which contributes most to the inaccuracy, unreliability and imprecise results. In terms of the three aspects being investigated, the major limitations of this technique are the reproducibility and the precision of the results as they show equal significance.

Ion Exchange and Acid-Base Titration Analysis

Ion exchange reactions involve the replacement of ions in solution with those in the solid, which are insoluble polymers manipulated into beads, referred to as the ion-exchange resins. There are many types of exchange resins of the natural and synthetic types, such as zeolites and 'permutits'.
Ion-exchange is used in industry to purify 'hard water'. Water is run through the column containing the resin in its sodium form and the water which contains dissolved magnesium and calcium salts is replaced with sodium ions:

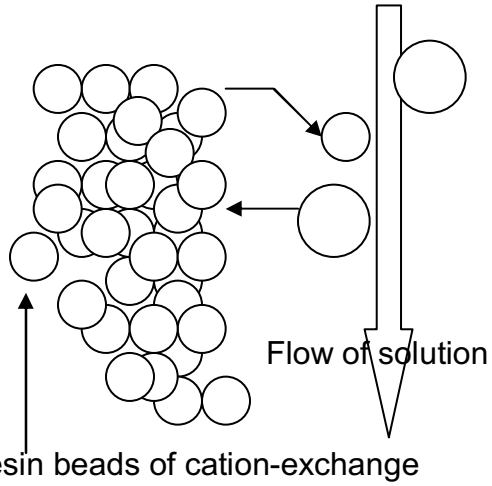
$$2\ \text{resin} - Na^{+}_{(s)} + M^{2+}_{(aq)} \qquad (\text{resin})_2 - M^{2+}(s) + 2Na^{+}_{(aq)}$$

which converts the hard water to 'soft water'.

This investigation involves the exchange of the copper^{2+} cations with hydrogen ions, meaning the resin will have to be in its hydrogen form.

$$2\ \text{resin} - H^{+}_{(s)} + M^{2+}_{(aq)} \qquad (\text{resin})_2 - M^{2+}(s) + 2H^{+}_{(aq)}$$

The cation-exchange resin has in it some reactive groups e.g. the sulphonic acid group $-SO_2OH$. I am going to run the solution of copper (II)sulphate through the ion-exchange column, which will replace the hydrogen ions of the sulphonic acid group with the copper^{2+} ions. The hydrogen ions which are removed from the resin then accumulate in the eluant and this solution can undergo an acid-base titration with sodium hydroxide to determine the concentration of hydrogen ions, which is proportional to the concentration of copper $^{2+}$ ions.
The reaction mechanism follows something like this:



The ion-exchange resin removes the copper 2+ ions from the unknown copper(II)sulphate solution and replaces them with hydrogen ions. The hydrogen ions are singly charged and therefore are held less strongly than doubly charged ions. The diagram across shows that one copper 2+ ion replaces two hydrogen ions, and is held more strongly due to its double charge.

When the hydrogen ions are hydrated, they hold many water molecules and so the force between the resin and the ions are weak, allowing the ions to wash out into the eluant.

When the resins have exchanged the hydrogen ions for the copper ions, the characteristic blue colour which appears in the beads is evidence of the fact that the exchange for copper ions has taken place. This analysis then involves the titration of the hydrogen ions that were released.

$$Cu^{2+}_{(aq)} \longrightarrow 2H^{+}_{(aq)}$$

The equation above shows that 1 mole of copper ions will replace 2 moles of hydrogen ions. The indicator that is ideal here is Phenolphthalein indicator solution as it goes from colourless to pink and this is a good practicable end-point to see.

Apparatus

- 250 cm^3 conical flask
- 10 cm^3 measuring cylinders
- burette
- gradated pipette
- clamp and stand
- beakers
- ion-exchange column with tap at bottom (1.5 cm x 25 cm)
- glass wool

Materials

- 30cm^3 strong cation-exchange resin (hydrogen form)
- phenolphthalein indicator
- 0.100 mol dm^{-3} sodium hydroxide solution
- 1.00 mol dm^{-3} ammonia solution
- copper(II)sulphate solution of unknown concentration

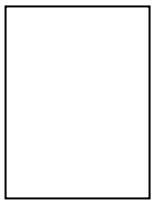
Justification of apparatus

The pipette is used to accurately measure 10 cm^3 of the unknown solution of copper sulphate as it is the standard volume of solution to be used.

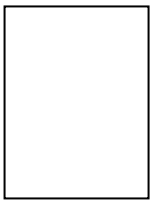
Glass wool is more ideal than cotton wool as the latter does not easily allow water through.

Phenolphthalein is used for the detection of the completion of the acid-base reaction between the replaced H^+ ions and OH^- ions.

Risk Assessment



Eye protection



Protective gloves

Sodium Hydroxide: **HARMFUL**[41]

WARNING! HARMFUL IF SWALLOWED. MAY CAUSE IRRITATION TO SKIN, EYES, RESPIRATORY TRACT AND GASTROINTESTINAL TRACT

If ingested: do not induce vomiting. Give large quantities of water. Seek medical attention immediately.
If inhaled: remove to fresh air. If breathing is difficult, give oxygen.
If splashed on skin: immediately flush skin with water for at least 15 minutes. Remove all contaminated clothing and seek medical attention if irritation persists.
If splashed in eyes: immediately flush eyes with plenty of water for at least 15 minutes, lifting upper and lower lids if necessary. Seek medical attention if irritation persists.

Disposal: salvage if there is a lot of solution remaining, if not then dilute the solution and dispose down the drain.

Hydrochloric acid: **CORROSIVE**[42]

DANGER! CORROSIVE. LIQUID AND MIST CAUSE SEVERE BURNS TO ALL BODY TISSUE. MAY BE FATAL IF SWALLOWED OR INHALED

In this investigation, concentrated solutions are not used so the potential health hazards do not require such radical health procedures. However, gloves and safety goggles must be worn.

[41] http://www.jtbaker.com/msds/englishhtml/s4038.htm
[42] http://www.jtbaker.com/msds/englishhtml/s4038.htm

Preparation of the solutions

Sodium hydroxide

Ready made 2M sodium hydroxide must be diluted to 0.1 mol dm^{-3}.

I. Accurately pipette 50 cm^3 of the sodium hydroxide and dilute to 100 cm^3.
II. Transfer this solution to a 1dm^3 flask, along with all the washings and dilute to the mark using distilled water.
III. Transfer to a bottle and label 0.1 mol dm^3 sodium hydroxide.

The **hydrochloric acid** is only used for the regeneration of the resin beads, and so it is readily available.

The Ion Exchange method

I. Obtain an ion-exchange column, sufficient glass wool to fill about 1.5cm at the bottom of the column, sufficient synthetic resin to fill the column.
II. Pour some of the unknown copper(II)sulphate solution into a beaker and keep aside.
III. Also, keep aside the 1mol dm^{-3} ammonia solution. This ammonia solution is for testing the eluant for any copper ions which it can complex with.
IV. Pack the bottom of the column with glass wool by tapping it down with a stirring rod.
V. Carefully, with a spatula, transfer 30 cm^3 of the resin to the column and make sure the tap on the bottom is closed.
VI. Set up and clamp and stand and secure the column vertically.
VII. Place a beaker under the column to collect the eluant and pour the copper sulphate solution of unknown concentration into the column.
Note: never let the column run dry, always keep the column full of solution. After all the copper sulphate solution has been poured, pour distilled water in place of the copper to keep the column wet.
VIII. Observe the colour change of the resin beads, the characteristic blue colour of the copper ions should be apparent in the beads and the eluent should be colourless. Wait for all the copper solution to be exchanged in the column.
IX. The resin beads have to be regenerated and this can be done by running a concentrated solution of hydrochloric acid through the column. The beads are now ready to be used again.
X. Set up the apparatus (steps V to VIII) and conduct the second trial.
XI. Keep the beakers containing the eluent aside for the titration.

The Titration

I. Set up a clamp and stand and place a burette in position.
II. Pipette 25 cm^3 of the eluent in the beaker to a clean conical flask.
III. Fill the burette with 0.10 mol dm^{-3} of the sodium hydroxide solution.
IV. Add three drops of the phenolphthalein indicator and initiate the titration.
V. Observe: the end-point is spotted by the permanent pink colour. The last remaining hydrogen ions left in the beads are exchanged rather slowly and so the pink colour in the conical flask disappears after a while. Keep the burette running until the pink colour persists.
VI. Repeat this procedure for the second eluent and record the burette readings.

Modifications to the method

The ion-exchange method involves a titration component and so the solutions involved must be dilute (1M). The copper sulphate solution of unknown concentration was diluted down to 0.1 mol dm^3 as in the complexiometric and redox titration analyses (see other methods).
If 10 cm^3 of the copper solution is used, then considering the stoichiometric ratio of the molarities, 1 mole of copper ions will replace 2 moles of hydrogen ions. So in theory, the burette reading should be roughly near 20 cm^3 upon reaching the end-point of the reaction.

Implementation

Results table for ion-exchange titration

	Titration trial			
	Rough	**T1**	**T2**	**T3**
Initial Burette reading (cm^3)	0	0	0	0
Final Burette reading (cm^3)	19.80	19.70	19.80	19.80
Final – Initial (cm^3)	**19.80**	**19.70**	**19.80**	**19.80**

Analysis

Now that the titration trials have been carried out, the concentration of the hydrogen ions can be determined using equation:

Number of moles = Concentration (mol dm^{-3}) x Volume (dm^3)

The concentration can be worked out by referring to the equation:

$Cu^{2+}_{(aq)} \longrightarrow 2H^{+}_{(aq)}$

The equation above shows that **one** mole of copper ions is displaced by **two** moles of hydrogen ions.

First all the volumes used must be converted to dm^3

$\frac{X}{1000}$ ← the volume (cm^3)

the conversion of cm^3 to dm^3

Titre values

Trial 1	Trial 2	Trial 3
$\frac{19.70}{1000}$	$\frac{19.80}{1000}$	$\frac{19.80}{1000}$
0.0197 dm^3	**0.0198 dm^3**	**0.0198 dm^3**

The volumes of copper sulphate added to the column

$\frac{10\ cm^3}{1000}$ = **0.01 dm^3**

Find the number of moles of copper in the 0.01 dm^3 of copper sulphate

0.01 dm^3 of copper sulphate solution displaces 0.0197 dm^3 of hydrogen ions for trial 1; 0.0198 dm^3 for trials 2 and 3.

$$n = C \times V$$

Trial 1

Concentration = 0.1 x 0.0197
= **0.00197 mol** of hydrogen displaced

-Since 2 moles of hydrogen displace 1 mole of copper ions, divide the value by two:

$$= \frac{0.00197}{2} = \textbf{0.000985 mol}$$ of copper in 0.01dm^3 of solution

Trial 2

Concentration = 0.1 x 0.0198
= **0.00198 mol** of hydrogen displaced

-Since 2 moles of hydrogen displace 1 mole of copper ions, divide the value by two:

$$= \frac{0.00198}{2} = \textbf{0.000990 mol}$$ of copper in 0.01dm^3 of solution

Trial 3

Concentration = 0.1 x 0.0198
= **0.00198 mol** of hydrogen displaced

-Since 2 moles of hydrogen displace 1 mole of copper ions, divide the value by two:

$$= \frac{0.00197}{2} = \textbf{0.000990 mol}$$ of copper in 0.01dm^3 of solution

Find the concentration of copper

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

A2 Chemistry

Cumulating the Overall Conclusions and Comparisons

The final conclusions made for all the techniques tested in this investigation must now be cumulated and compared in terms of their relative effectiveness by comparing them on which technique gives rise to the most **reliable** results, which technique enables the utmost **precise** results and above all which technique is paramount when considering the **accuracy** of the results.