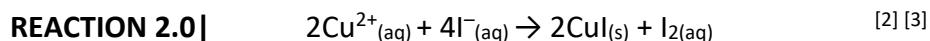


Analysis of the copper analyte solution by an iodometric (redox) titration

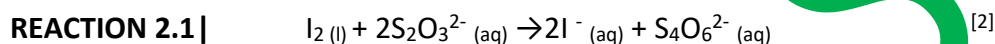
This section describes the chemistry behind a redox titration that can be used to obtain data to calculate the percentage of copper in the one pence piece. Samples of 25cm³ of the copper(II) analyte solution will be analysed.

Potassium iodide solution is added to a sample of the copper(II) analyte solution. This results in a redox process that produces copper(I) iodide and iodine ^[1]. Copper (II) ions are reduced and iodide ions are oxidised. The iodine in solution will turn the solution a brown colour and the copper(I) iodide will precipitate out of solution as it is insoluble, forming a white suspended solid that clouds the solution ^[2]. Overall the solution will appear as a thick, creamy, brown colour.



Stage two:

An iodometric redox titration using sodium thiosulfate solution and a starch indicator can then be conducted to calculate the concentration of iodine formed ^[3] and hence, indirectly, the amount of Cu²⁺_(aq) ions that were present in the sample of copper(II) analyte solution.



The solution will initially have a creamy precipitate and appear brown due to the iodine ^[4]. As thiosulfate is added, iodine is reduced and so near the endpoint, the solution will turn a straw colour. Starch indicator is added, turning the solution blue-black as a starch-iodine complex forms ^[3]. More thiosulfate is added until the solution is no longer brown and is solely white, the endpoint.

Starch indicator is added close to the endpoint to give a sharp endpoint while avoiding the formation of excess starch-iodine complex, which would be difficult to decompose. The starch indicator must be freshly prepared so that its accuracy is not degraded.

How much iodide solution needs to be added?

Value	Calculation	Result
Theoretical moles of copper(II) ions in the 500 cm ³ analyte solution.	$\frac{3.4532\text{g}}{63.546\text{ g/mol}}$	0.05434... mol
Theoretical concentration of copper(II) ions in the 500 cm ³ analyte solution	$\frac{0.05434 \dots \text{mol}}{0.5 \text{ dm}^3}$	0.1086... mol dm⁻³ (3 s.f.)
Theoretical moles of copper(II) in a 25cm ³ sample of copper analyte	$\frac{0.05434 \dots \text{mol}}{20}$	0.002717... mol
Minimum moles of iodide ions required in reaction 2.0	$4 \times \frac{0.002717 \dots \text{mol}}{2}$	0.005434 ... mol

Table 2.0: Expected concentration of copper(II) analyte solution and the amount iodide to be added.

Given that the limiting factor in **reaction 2.0** is the moles of copper(II), excess iodide ions must be added to ensure all copper(II) ions are reduced to copper(I). No matter how much excess iodide ions are present, the amount of iodine formed in the reaction is dependent on the original moles of copper(II) present.

An excess of iodide solution should be added ^[1] but the moles required is so low that a very small concentration is required. A common dilute concentration is 0.5M. The volume of potassium iodide should be small enough to be measurable by a single 50cm³ burette but not too small as this increase the uncertainty of the burette measurement. A **concentration of 0.5M** can be justified by further calculation.

Value	Calculation	Result
Minimum volume of potassium iodide required in reaction 2.0	$\frac{0.005434 \dots \text{mol}}{0.5}$	0.010868... dm³ = 10.9 cm³

Table 2.1: In order to add excess potassium iodide, a volume of 15cm³ 0.5M potassium iodide is appropriate

The volume of potassium iodide does not have to be accurate since the analytical calculations are only dependant on the amount of iodine formed, which in turn is dependent on the moles of copper(II) present - **provided iodide is added in excess.** ^[2]

How much sodium thiosulfate solution needs to be added?

Value	Calculation	Result
Theoretical moles of copper(II) being reduced in a 25cm ³ sample of copper analyte	$\frac{0.05434 \dots \text{mol}}{20}$	0.002717... mol
Moles of iodine formed during reaction 2.0	$\frac{0.002717 \dots \text{mol}}{2}$	0.0013585... mol
Moles of thiosulfate ions required in reaction 2.1 to oxidise iodine	$2 \times 0.0013585 \dots \text{mol}$	0.002717... mol
For a concentration of 0.1M sodium thiosulfate solution, the theoretical volume required in the titration is...	$\frac{0.002717 \dots \text{mol}}{0.1}$	= 0.02717dm³ = 27.2 cm³ (3 s.f.)

Table 2.1: Calculating the amount of sodium thiosulfate required. A quantity of ~27.2cm³ at 0.1M is required per titration

Reactions 2.0 and 2.1 indicate that the moles of copper (II) present is equal to the moles of thiosulfate required to oxidise the iodine. 0.1M is a justified concentration to use since it is easy to make a standard solution of 0.1M sodium thiosulfate. Moreover, the concentration is such that the volume used in the titration will be ~ 27cm³, which is large enough for an accurate reading using a burette but still small enough to fit in a 50cm³ burette.

Practical technique B: Transferring a solution using a pipette and suction filter

After rinsing the volumetric pipette with distilled water, apply a suction filter to the widest end and draw up some (< 10cm³) of the desired solution. Hold the volumetric pipette over a sink drain and remove the suction filter but immediately cover the end where the filter was with your finger to cause a vacuum so the solution does not leave the volumetric pipette. Invert the volumetric pipette several times to rinse the inside of it with the solution.

Then reapply a suction filter to the widest end and draw up some of the desired solution so the level exceeds the volumetric marking on the pipette. Remove the suction filter and immediately cover the end where the filter was with your finger to cause a vacuum so the solution does not leave the pipette. Then facing the pipette head on, to reduce parallax error, slowly lift your finger with minute movements as to lower the solution level in the pipette until the bottom of the meniscus is in line with the volumetric marking of the pipette. Then hold the pipette above the desired apparatus which you wish to transfer the solution into and release your finger. Allow the solution to run out the pipette and then gently touch the tip of the pipette against the surface of the solution you have transferred it to. ^[4]

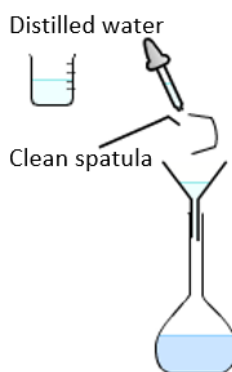
Method 2.0 – Making 0.5M potassium iodide solution

A solution of 0.5M potassium iodide solution is required. In the lab, potassium iodide is available as an anhydrous white solid. The titration will be repeated a further three times for concordant results. This means that at least 60cm³ 0.5M potassium iodide solution is required.

Value	Calculation	Result
Concentration of KI _(aq)	0.5 M	
Volume of KI _(aq)	(100cm ³ = 0.100 dm ³)	
Moles of KI _(s)	0.5M X 0.100 dm ³	0.050 mol
Mr of KI _(s)	166.00277 gmol ⁻¹ [5]	
Mass of KI_(s) to be dissolved	166.00277 gmol ⁻¹ X 0.050 mol	8.30g (to nearest 0.01g)
Equipment / reagents		Extra details
Eye protection and lab coat		
Sensitive digital balance		Accurate to 0.01g
Plastic weighing boat		This should be brand new
2 X clean stainless steel spatulas		Rinsed with distilled water and dried with some paper towel
Small clean funnel		Rinsed with distilled water and dried with some paper towel
100cm ³ volumetric flask with stopper		Rinsed with distilled water and dried with some paper towel
Potassium iodide powder		Anhydrous KI _(s) powder
Distilled water		In a clean 'wash bottle'
Clean dropper pipette		Rinsed with distilled water.



Measuring out 8.30g of potassium iodide powder with a digital balance (accurate to 0.01g).



Transferring potassium iodide to a 100cm³ volumetric flask using a funnel, clean spatula and distilled water. Rinse the funnel and spatula into the volumetric flask to transfer all washings using distilled water.

100cm³ 0.5M potassium iodide solution

Diagrams made using Microsoft Word 2013 & 'Chemix online', <http://chemix.org/>, developed by Micron developers, © 2007-2017.

1. Place a plastic weighing boat onto the digital balance and zero the balance.
2. Weigh out 8.30g of KI_(s) powder into the weighing boat using a spatula (measuring to the nearest 0.01g).
3. Carefully remove the weighing boat from the scales and empty the powder into the 100cm³ volumetric flask using a funnel if necessary to ensure that no powder is lost. Lightly tap the bottom of the weighing boat and scrape out any powder using a clean spatula. Ensure that the end of the spatula is also tapped on the inside of the funnel.
4. Using a wash bottle of distilled water, carefully wash the inside of the funnel, weighing boat and spatula end into the volumetric flask. Continue to add distilled water to make the solution up to mark.

Note: When making the volumetric flask up to mark, refer to **practical technique A**

- Place a stopper on the volumetric flask containing the potassium iodide solution and invert several times to ensure the solution is homogeneous.

Method 2.1 – Making 0.1M sodium thiosulfate solution ^{[5],[6]}

Sodium thiosulfate is available as a hydrated white solid/crystalline granules in the lab. It is sometimes referred to as sodium thiosulfate pentahydrate and has the formula $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$. The molecular weight of this compound is **248.181 gmol⁻¹**. ^[5]

A 0.1M solution of sodium thiosulfate is to be made. The titration will be repeated at least 3 times for concordant results (titres within a range of 0.10cm^3). This means that at least 120cm^3 of 0.1M sodium thiosulfate is required to be synthesized.

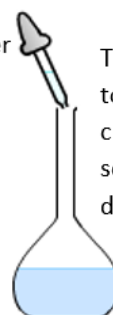
Value	Calculation	Result
Concentration of $\text{Na}_2\text{S}_2\text{O}_3$ (aq)	0.1 M	
Volume of $\text{Na}_2\text{S}_2\text{O}_3$ (aq)	$(250\text{cm}^3 = 0.250 \text{ dm}^3)$	
Moles of $\text{Na}_2\text{S}_2\text{O}_3$ (s)	$0.1\text{M} \times 0.250 \text{ dm}^3$	0.025 mol
Mr of hydrated $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (s)	248.1841386 gmol⁻¹ ^[5]	
Mass of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (s) to be dissolved	248.1841386 gmol⁻¹ X 0.025 mol	6.20g (to nearest 0.01g)

Equipment / reagents	Extra details
Eye protection and lab coat	
Sensitive digital balance	Accurate to 0.01g
Plastic weighing boat	This should be brand new
Clean stainless steel spatula	Rinsed with distilled water and dried with some paper towel
250cm^3 volumetric flask with stopper	Rinsed with distilled water and dried with some paper towel
Solid sodium thiosulfate crystals	Hydrated $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (s) crystals
Distilled water	In a clean 'wash bottle'
Clean dropper pipette	Rinsed with distilled water.



Measuring out 6.20g of hydrated $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (s) crystals with a digital balance (accurate to 0.01g).

Distilled water



Transferring hydrated $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (s) to a 250cm^3 volumetric flask using a clean spatula and distilled water. The solution is made up to mark with distilled water.

Diagrams made using Microsoft Word 2013 & 'Chemix online', <http://chemix.org/>, developed by Micron developers, © 2007-2017.

- Place a plastic weighing boat onto the digital balance and zero the balance.
- Weigh out 6.20g of hydrated $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (s) crystals into the weighing boat using a spatula (measuring to the nearest 0.01g).
- Carefully remove the weighing boat from the scales and pour the crystals into the 250cm^3 volumetric flask. Lightly tap the bottom of the weighing boat to ensure all crystals enter the flask.

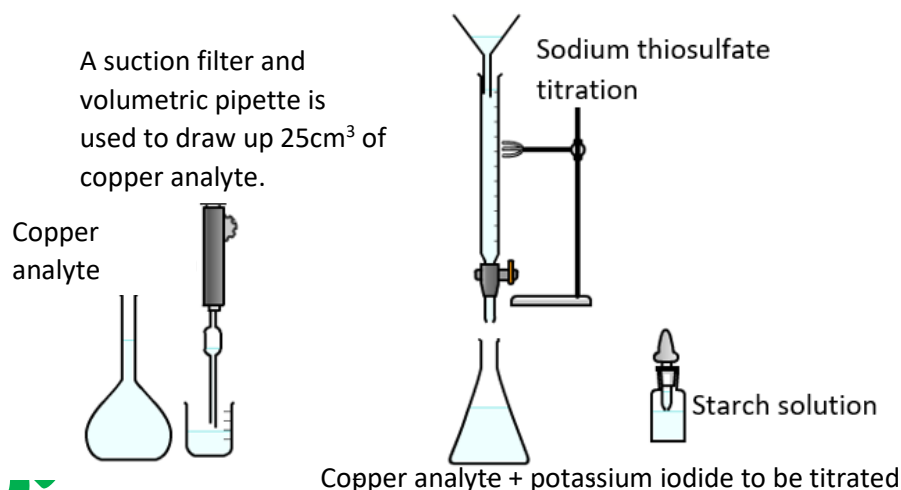
Using a wash bottle of distilled water and a dropper pipette, make the solution up to mark.

Note: When making the volumetric flask up to mark, refer to **practical technique A**

- Place a stopper on the volumetric flask containing the 0.1M sodium thiosulfate solution and invert several times to ensure the solution is homogeneous.

Method 2.2 – Redox titration to determine the copper(II) concentration ^{[6],[2],[1]}

Equipment / reagents	Extra details
Eye protection and lab coat	
0.1M sodium thiosulfate solution	From method 2.1
0.5M potassium iodide solution	From method 2.0
Copper analyte solution (from method 1.2)	Stoppered and stored in a fume cupboard.
2X 50cm ³ burettes	To be rinsed with distilled water and a small quantity of the solution they will hold.
2 sets of clamp stands, clamps and bosses	Securely mounted to hold a burette vertically.
2 X small funnels	To be rinsed with distilled water and a small quantity of the solution they will hold.
White card	To read glassware scales with accuracy.
25cm ³ pipette with a suction filter	To be rinsed with distilled water and a small quantity of the solution it will hold.
250cm ³ conical flask	Rinsed with distilled water.
Distilled water	Contained in a clean wash bottle
Starch solution	
Dropper pipette with a 5ml graduated scale	Rinsed with distilled water.
0.2% (w/v) starch solution starch solution	"Freshly prepared"



Diagrams made using Microsoft Word 2013 & 'Chemix online', <http://chemix.org/>, developed by Micron developers, © 2007-2017.

- Rinse a 50cm³ burette with distilled water and then some 0.5M potassium iodide solution. Mount the burette vertically with a clamp stand, clamp and boss. Fill the burette with 0.5M potassium iodide solution and allow some to run out of the tap to displace any air. A small funnel may be required. This should be rinsed with distilled water and a small quantity of the solution being transferred.
- Rinse a 50cm³ burette with distilled water and then some 0.1M sodium thiosulfate solution. Mount the burette vertically with a clamp stand, clamp and boss. Fill the burette with 0.1M sodium thiosulfate solution and allow some to run out of the tap to displace any air. A small funnel may be

required. This should be rinsed with distilled water and a small quantity of the solution being transferred.

- The 25cm³ pipette should be rinsed with distilled water. Then rinse it with a small quantity of the copper analyte solution using the technique described in **practical technique B**.

Follow **practical technique B** in order to transfer 25cm³ of the copper analyte solution into a clean 250cm³ conical flask.

- Place the conical flask containing the 25cm³ of the copper analyte solution beneath the potassium iodide burette and run 15cm³ of 0.5M potassium iodide into the solution. The initial reading on the burette is read and the final reading will be 15cm³ on from this. The burette is read to the nearest 0.05cm³ (reading the scale from the base of the meniscus of the solution level), **but accuracy is not essential for this step**.

- The liberated iodine in the conical flask from the previous step is titrated using the sodium thiosulfate solution. To do this, place the conical flask beneath the burette containing the 0.1M sodium thiosulfate solution. Record the initial volume on the burette to the nearest 0.05cm³. A white card may be held behind a burette to make the volume readings more easy to judge. The scale should be faced head on to reduce parallax error.

- Run the 0.1M sodium thiosulfate solution into the conical flask, gently swirling the conical flask, ensuring the mixture does not make its way up the inner sides of the flask. Distilled water may be added if this occurrence is to happen as it does not affect the endpoint of the titration. Continue to run the sodium thiosulfate solution into the conical flask but slow down the tap by closing it slightly to a dropwise succession, as the solution begins to turn a clearer straw colour. Near the endpoint (say ~27cm³), the solution in the conical flask turns a straw colour.

A few drops of starch solution (<5ml) are then added to the conical flask using a dropper pipette with a scale (accuracy is not essential but the quantity should be kept consistent for each titration). This will turn the solution a blue-black colour. The titration continues (running in a dropwise succession) until the solution becomes colourless, indicating the endpoint. The initial volume, final volume and titre are recorded to the nearest 0.05cm³.

- Repeat steps 3 to 6 (and refill the burettes if necessary) so that at least three concordant results are obtained.

The burette with the sodium thiosulfate solution will need to be refilled after each titration. The conical flask must be cleaned with distilled water and solutions are discarded down the drain after each titration.

- The mean titre of sodium thiosulfate is used with its known concentration (0.1M) and Mr (248.1841386 gmol⁻¹ [5]) to calculate the moles of copper (II) ions in the 25cm³ sample and then scale this up to account for the total 500cm³ volume of the analyte solution, thus the moles of copper in the one pence piece. Using the molecular mass of copper and the total moles of copper in the coin, the mass of copper present in the coin can be calculated. A percentage is then made relative to the mass of the original coin. The percentage mass is then compared to the percentage mass of copper in a standard pre-1992 one pence piece as published by the Royal Mint.

Risk Assessments for section 2.0

Risk	Hazard	Precaution	Source ID
Copper analyte (Cu ²⁺ , Sn ²⁺ , Zn ²⁺ , NO ₃ ⁻ , H ⁺)	Acidic solution and nitrates present have oxidising properties so can cause violent reactions with reducing agents.	Wear eye protection and a protective lab coat.	1
		Wash skin well if in contact.	3
		The solution should be kept in a fume cupboard encase any further oxidation occurs to release toxic nitrogen dioxide or nitrogen oxide if the solution is dilute.	4

	Copper (II) nitrate is harmful if ingested and can irritate the eyes and skin. Zinc ions in solution are harmful and compounds can be an irritant to the skin.	Spills on tabletops, floors etc. should be flooded with water and mopped up. Large spills should be cleared using a mineral absorbent. Do not inhale or ingest. Keep away from reducing agents and other chemicals not needed in the practical. Keep away from any naked flames to prevent toxic fumes.	
0.2M sodium thiosulfate solution	Low Hazard. This may form sulfur or sulfur dioxide (a toxic gas) if reacted with acid. Sulfur dioxide gas is poisonous and irritates the eyes and lungs. However, it is very soluble in water. In solution, it poses a low hazard.	The lab should be well-ventilated and fumes should not be inhaled. Avoid skin contact and do not ingest the solution. Wear protective goggles and a lab coat. Do not expose asthmatics to any fumes that evolve. If sodium thiosulfate is spilt on skin, rinse with water and dry. If sodium thiosulfate is spilt on the floor then mop up with a damp cloth and rinse the area well.	2 5
0.2% (w/v) starch solution	Low hazard	If spilt on the floor, mop up using a damp cloth. If spilt on the skin, then rinse with water.	6
Iodine	Harmful if ingested or inhaled. Harmful to the skin, causing severe burns if left for some time.	Do not inhale or ingest. Keep away from naked flames. Ensure the lab is well ventilated. Wear eye protection and a protective lab coat. If in contact with the skin then immerse in sodium thiosulfate solution (20%, 1 M) and then drench with plenty of water. See a doctor if a large area is affected or blistering occurs. If spilt on the floor, scoop up any iodine solid, add sodium thiosulfate solution (20%, 1 M) then dilute with plenty of water and mop up with a damp cloth.	7
Potassium iodide powder and solution (0.5M)	Low hazard – similar effects to sodium chloride. May cause dehydration and high blood pressure. Fine powder may be irritating to the respiratory system.	Do not ingest. Do not inhale the fine powder. If in contact, wash hands with water. Wear eye protection. If spilt on the floor, dilute with plenty of water and mop up with a damp cloth.	8
Hydrated sodium thiosulfate crystals and solution (0.1M)	Low hazard – They produce sulfur and sulfur dioxide when in reacted with acids.	Do not ingest. Wear eye protection. Wash hands if in contact. Keep away from strong acids. Use in a well-ventilated lab and keep the bottle stoppered when not in use.	9
Copper iodide	Low hazard – see potassium iodide	See potassium iodide	8

Source ID	Institute/name	URL/link	Year
1	CLEAPSS	CLEAPSS Hazcard: 21 Nitric (V) acid, www.cleapss.org.uk /resource/Student-Safety-Sheets-ALL.pdf	2017
2	CLEAPSS	CLEAPSS Hazcard: 35 Sodium sulfites, thiosulfate & persulfate, www.cleapss.org.uk /resource/Student-Safety-Sheets-ALL.pdf	2017
3	CLEAPSS	CLEAPSS Hazcard: 40 Copper and its compounds, www.cleapss.org.uk /resource/Student-Safety-Sheets-ALL.pdf	2017
4	CLEAPSS	Hazcard 49: Zinc & its compounds, www.cleapss.org.uk /resource/Student-Safety-Sheets-ALL.pdf	2017
5	CLEAPSS	Hazcard 52: Sulfur dioxide, www.cleapss.org.uk /resource/Student-Safety-Sheets-ALL.pdf	2017
6	CLEAPSS	Hazcard 64: Carbohydrates, www.cleapss.org.uk /resource/Student-Safety-Sheets-ALL.pdf	2017
7	CLEAPSS	Hazcard 56: Iodine, www.cleapss.org.uk /resource/Student-Safety-Sheets-ALL.pdf	2017
8	CLEAPSS	Hazcard 56: Iodine, www.cleapss.org.uk /resource/Student-Safety-Sheets-ALL.pdf	2017

9	CLEAPSS	Hazard 35: Sodium sulfites, thiosulfate & persulfate, www.cleapss.org.uk/resource/Student-Safety-Sheets-ALL.pdf	
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References for section 2.0

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