

INVESTIGATING THE PERCENTAGE OF COPPER IN A ONE PENNY COIN (1971-1992)

BACKGROUND

The 1971-1992 One Penny coin, according to the publication of the Royal Mint, contains 97% copper, 2.5% zinc and 0.5% tin, an alloy sometimes referred to as 'coinage bronze'. The published mass of the One Pence coin is 3.56g .

The aim of this investigation is to verify this claim by experimentally determining the copper content of a 1971-1992 One Penny sample.

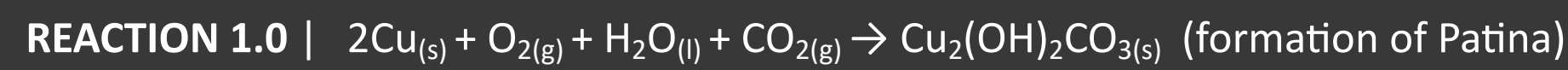
The investigation employs two independent analytical techniques, namely an iodometric titration and a second based on electrochemical measurements from Daniel cells of different half-cell concentrations.

Two analytical methods are used as this allows a comparison of the accuracy of each method. Moreover, the second method is present to decipher whether the experiment is reproducible or error prone.

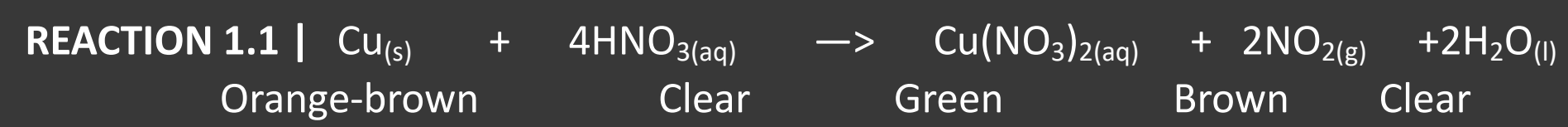
METHOD

Making an analyte solution

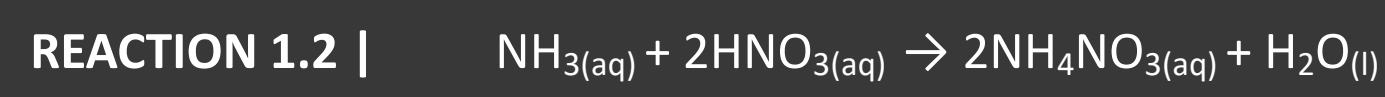
Preparation stage one: Cleaning the copper coin. The pre-1992 copper coins are cleaned using emery cloth and an ethanol solution. This is to remove any surface impurities the coin may have collected and to remove the outer surface of Verdigris (patina). Verdigris is a bright bluish-green compound found on the surface of copper coins and forms due to oxidation in moist air:



Preparation stage two: Liberating the copper(II) ions from the coin using excess nitric(V) acid. A solution of copper(II) ions of unknown concentration is formed by the process:



Preparation stage three: The solution is neutralised to remove any excess nitric(V) acid (an oxidising agent) which could interfere with the redox processes involved in the analytical methods. A solution of ammonia is used as this does not form an insoluble precipitate, so the copper(II) ions remain in solution.



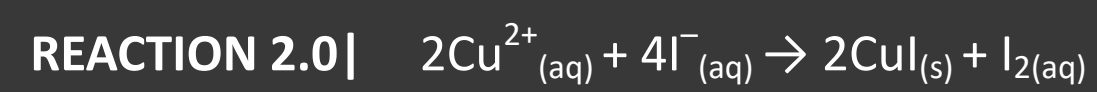
The solution has a deep blue colour due to the ligand $[\text{Cu}(\text{NH}_3)_4](\text{NO}_3)_2$ forming. However, this means copper(II) ions are liberated from the coin and are present homogeneously through the solution.

Preparation stage four: The solution is made up to 500 cm³ in a volumetric flask using distilled water. This results in a copper analyte solution of unknown concentration.

Analytical method one — The Iodometric Titration

25 cm³ samples of the copper(II) analyte solution are analysed. These are taken from the 500 cm³ analyte solution using a 25 cm³ volumetric pipette with a pipette filter.

Stage one: Potassium iodide solution is added in excess to each sample of copper(II) analyte solution. This results in a redox process which forms copper(I) iodide and iodine. Iodine causes the deep-blue solution to turn a brown colour. Moreover, copper(I) iodide precipitates out of solution as a white suspension making the solution cloudy.



A small quantity (~10cm³) of hydrochloric acid is added to the solution since it catalyses the oxidation of the iodide ion to iodine.

Stage two: A redox titration using 0.1 M sodium thiosulfate solution and a starch indicator is conducted. The sodium thiosulfate is added to the analyte solution until the solution becomes a lighter creamy-straw colour (i.e. before the end point). A few drops of starch are added to turn the solution a blue-black colour (indicating the presence of iodine). The addition of sodium thiosulfate is continued, at a dropwise succession, until the straw colour vanishes and the solution turns white. The titre of sodium thiosulfate is then used to calculate the amount of copper(II) ions present in the sample of copper analyte solution.



Starch indicator is added, until the solution turns blue-black as a starch-iodine complex forms with iodine. Starch indicator is added close to the endpoint to give a sharp endpoint while avoiding the formation of excess starch-iodine complex, which is difficult to decompose. A fresh starch solution is made up for the titration beforehand, as starch decomposes and loses its sensitivity in iodometric titrations.

IODOMETRIC TITRATION RESULTS AND ANALYSIS

Burette reading	Rough	Titre 1	Titre 2	Titre 3	Titre 4	Titre 5	Titre 6
Initial / cm ³	0.00	1.95	4.00	0.35	4.30	0.55	0.00
Final / cm ³	27.85	28.40	31.10	26.75	30.95	27.00	26.45
Titre / cm ³	27.85	26.45	27.10	26.40	26.65	26.45	26.45
Average / cm ³	26.4375	= 26.44 (2 d.p.)					
Absolute uncertainty	+/- 0.05 cm ³	Found by dividing the range shown by the concordant results by 2					
Percentage uncertainty	0.19 %						

Titres 1, 3, 5 and 6 showed concordance within 0.10 cm³ (i.e. the readings were within the absolute uncertainty of a given measurement from a burette). These titres were used to calculate the mean titre of 26.44 cm³ of 0.1 M sodium thiosulfate. The absolute uncertainty of this mean value is found by dividing the range the values used to form the mean (titres 1, 3, 5 and 6) by 2, giving an absolute uncertainty of +/- 0.5 cm³, corresponding to a percentage uncertainty of 0.19%.

This mean titre was used to calculate the percentage of copper in the coin and the error associated with this judgement can be found on pages 4 and 5 of the "Copper coin analysis reference booklet".

This analysis shows that the experimentally determined percentage mass of copper in the coin was 99.2%. This value is 2.2% higher than the value published by the royal mint (97%).

The uncertainty in the experimentally determined value with respect to the resolutions of the equipment was calculated as +/-1.04%.

This means that the experimentally determined percentage of copper in the coin lies between 98.12% and 100.23%. The range does not coincide with the expected copper content of 97%. This is potentially due to a systematic error in the chemical technique. The sources of uncertainty and potential systematic errors are discussed in detail on pages 1 and 2 of the "Copper coin analysis reference booklet".

ANALYTICAL METHOD TWO - ELECTROCHEMICAL POTENTIALS

A 50 cm³ sample of the copper(II) analyte solution was analysed to find its concentration. A collection of electrochemical 'Daniel cells' were made using a range of different concentrations of copper (II) solution.

The Daniel cell is an electrochemical cell consisting of a zinc electrode in a zinc sulfate solution (of known concentration) and a copper electrode in a copper(II) sulfate solution, linked by a salt bridge.

Some filter paper was submerged in a concentrated solution of potassium nitrate(V) to form the salt bridge. Potassium ions and nitrate(V) ions carry current in the salt bridge so there is electrical contact between the two solutions but no mixing. Theoretically there should be an infinite resistance between the two electrodes but this is not achievable in the laboratory. The electrical potential ('E_{cell}') between these two half cells is measured using a high-resistance voltmeter so that negligible current flows between the half-cells' electrodes.

The copper half-cell is more positive than the zinc half-cell. This means that Cu²⁺ ions are reduced to copper and zinc is oxidised to Zn²⁺ ions. The concentration of Zn²⁺ in the zinc half-cell increases and so nitrate ions (NO³⁻) migrate from the salt bridge into the zinc half-cell. Conversely, the concentration of Cu²⁺ in the copper half-cell reduces, so potassium ions (K⁺) migrate from the salt bridge into the copper half-cell.

A standard solution of 0.5 M zinc sulfate was created for use in the negative (zinc) half-cells. A standard solution of 0.4 M copper(II) sulfate solution was made and dilutions were carried out to form less concentrated solutions of copper(II) sulfate solution (0.40, 0.30, 0.20, 0.11 and 0.1 M) through the use of a burette of distilled water and a burette of the standard 0.4 M copper(II) solution.

Some of the unused 0.4 M copper(II) sulfate standard solution was used in a serial dilution to form a 0.1 M standard solution of copper(II) sulfate which was used to create less concentrated solutions of copper(II) sulfate (0.09, 0.08, 0.07 and 0.6 M) through the use of a burette of distilled water and a burette of the standard 0.1M copper(II) sulfate solution. The Daniel cell was set up for each different concentration of copper(II) with a separate standard 0.5 M zinc sulfate half-cell after each E_{cell} measurement. All metals strips were rinsed and dried before use in different half-cells to avoid contamination.

The electrochemical potentials are plotted on a graph against the natural log of the ratio between the concentration of Zn²⁺ ions in the negative cell and the concentration of Cu²⁺ ions in the positive cell (i.e. $\ln\left(\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}\right)$). A line of best fit is then plotted and the electrochemical voltage of the copper(II) analyte Daniel cell can be plotted onto the calibration line to find the value of $\ln\left(\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}\right)$ and hence by rearranging, the concentration of copper(II) in the analyte sample. The justification for the relationship between the ion concentration and the measured electrochemical cell potential is defined by the **Nernst equation**:

- E_{cell} = the measured cell potential (V) between two half cells
- E_{cell}^o = the cell potential (e.m.f) published using standard conditions (V) between two half cells
- R = The Gas constant, 8.314 Jmol⁻¹K⁻¹
- T = The temperature in kelvin, room temperature (298K) or directly measured
- n = the moles of electrons, e⁻¹, given by the balanced redox reaction
- F = Faraday's constant, 96,485 Cmol⁻¹
- Q = The reaction quotient

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \left[\frac{RT}{nF} \right] \ln Q$$

A plot of electrochemical potentials against lnQ follows the relation given by the Nernst equation. The gradient should thus equal -(RT/nF), since E_{cell} is linearly related to lnQ.

The reaction quotient, Q, is dependent on the relative amounts of reactants and products present during a reaction at a given time. For the Daniel cells used, the reaction quotient is approximately equal to the value of $\ln\left(\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}\right)$.

During the experiment, the electrochemical potentials were recorded at a temperature of ~22°C (295 K). The concentration of the zinc half-cells were always ~0.5 M.

The calibration curve gives a value of lnQ for the copper(II) analyte solution based on the measured electrochemical potential.

Therefore, to find the concentration of copper(II): $\ln Q = \ln\left(\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}\right) \rightarrow Q = \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \rightarrow [\text{Cu}^{2+}] = \frac{[\text{Zn}^{2+}]}{Q}$, where Q is found by the calculation e^{lnQ}.

Concentrations of copper(II) were used in the half-cells which were both above and below the predicted concentration of the copper(II) analyte solution (0.106 mol dm⁻³), in order that the calibration line could be used to interpolate a value. Thus a less accurate extrapolation of the calibration line was avoided, which would have been the case if the concentrations being analysed had all fell either side of the concentration of the analyte solution.

ELECTROCHEMICAL POTENTIAL RESULTS AND ANALYSIS

Results from the Daniel Cell

Cells 5 and 6 proved to be anomalies since their average cell voltage did not fit the trend in the results and so they were excluded from the formation of the calibration trend line on the graph found on page 6 of the "Copper coin analysis reference booklet".

Plotting the average cell potentials against the value of $\ln Q \sim \ln\left(\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}\right)$ showed a linear trend line with a constant negative gradient. This was expected from the Nernst equation ($E_{\text{cell}} = E_{\text{cell}}^{\circ} - (RT/nF)\ln Q$) which suggests the gradient of the plot: $E_{\text{cell}} / \ln Q = -(RT/nF)$.

Using the gradient of the plot and the E_{cell} value for the 50 cm³ sample of copper(II) analyte solution used in the Daniel cell, the corresponding value for lnQ is equal to "1.5324...". Given that the concentration of the 50 cm³ zinc half-cell was 0.5 M, the experimentally determined concentration of the copper(II) analyte solution is calculated as 0.108 mol dm⁻³ (3 s.f.) (See pages 3, 7 and 8 of the "Copper coin analysis reference booklet" for calculation methods.)

This shows that the experimentally determined percentage mass of copper in the coin by this method was 101% (3 s.f.). This value is 4.0% higher than the value published by the royal mint (97%). The uncertainty in this experimentally determined value was calculated as +/-10%. The uncertainty in the experimentally determined copper content does account for the percentage difference and so it is possible that the royal mints' publication are consistent with the experimental result. The uncertainty of the copper content calculated and the sources of error for this method are analysed in detail on pages 1 and 2 of the "Copper coin analysis reference booklet".

Cell ID	Concentration of copper(II) / moldm ⁻³	Concentration of zinc(II) / moldm ⁻³	ln(Q) ~ ln([Zn ²⁺]/[Cu ²⁺])	Electrochemical potential, E _{cell} / V			
				Reading 1	Reading 2	Reading 3	Average
1	0.4	0.5	0.223143551	0.762	0.763	0.766	0.764
2	0.3	0.5	0.510825624	0.763	0.759	0.764	0.762
3	0.2	0.5	0.916290732	0.748	0.750	0.752	0.750
4	0.11	0.5	1.514127733	0.741	0.746	0.747	0.745
5	0.1	0.5	1.609487912	0.740	0.742	0.745	0.742
6	0.09	0.5	1.714798428	0.740	0.741	0.749	0.743
7	0.08	0.5	1.832581464	0.738	0.731	0.735	0.735
8	0.07	0.5	1.966112856	0.741	0.738	0.744	0.741
9	0.06	0.5	2.120263536	0.735	0.739	0.738	0.737
A	Unknown	0.5 ln(0.5/[Cu ²⁺])		0.746	0.743	0.745	0.745

CONCLUSIONS AND EVALUATION OF METHODS

Both the iodometric titration and the electrochemical analysis resulted in an overestimate of the copper content of the pre-1992 coin. The iodometric titration had a smaller percentage uncertainty of 1.04% in the experimentally determined copper content and so showed a higher precision than the electrochemical analysis which had a 10% percentage uncertainty.

However, the range in the copper content found by the electrochemical analysis of 101% +/- 10% does agree with the Royal Mint's published 97% content.

In reality, the copper content could not exceed 100% and so the overestimate is a facet of the precision of the measurement and may have an additional systematic error.

The electrochemical analytical technique is prone to more error than the titration, particularly with random fluctuations in the electrical potential readings caused by varying resistance. It is hard to control the internal resistance of each electrochemical cell (due to the saturation of the salt bridge, length of salt bridge, distance between the submerged areas of the electrodes and salt bridge etc.).

Moreover, the electrochemical potentials must be recorded as fast as possible once the salt bridge is added and the voltmeter is applied across the electrode terminals. This is because the redox reactions will take place as soon as some current can flow between the cells and across the salt bridge. This results in the concentration of Zn²⁺ in the zinc half-cell increasing and the concentration of Cu²⁺ in the copper half-cell decreasing. Three recordings of electrochemical potential were recorded in a short interval of time for each Daniel cell used in the electrochemical analysis. An average was made and any anomalies were excluded from the trend line on the calibration graph.

The iodometric titration proves to be less susceptible to random error and its systematic error can be reduced by taking care in the practical technique and using higher resolutions on practical equipment.

Systematic error in the titration resulted in an overestimate of the copper content. This is most significantly because of the judgement of the endpoint of the titration since the uncertainty created by the apparatus was very small (+/- 1.04% overall) and did not account of the percentage difference with respect to the Royal mint's published copper content.

In order to improve this investigation, the iodometric titration could be repeated more times to get a wider data set and the electrochemical technique should use a higher quality of half-cell construction (using quantitative measurements to maintain the distances between components of the half-cell etc.).

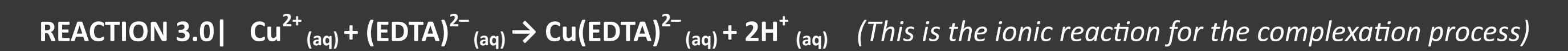
Overall, the investigation is reproducible given that there was only a 1.8% difference between the two experimentally determined copper content percentages which is justified by the errors and uncertainty analysed in details over pages 1 & 2

AN ALTERNATIVE METHOD FOR THE INVESTIGATION

A complexometric titration could be conducted rather than an iodometric titrations since the endpoint would be easier to judge given the lack of creamy precipitate (e.g. copper iodide) seen in the iodometric titration. This could improve the accuracy of the analysis of the copper(II) analyte concentration.

Ligands split the outer-shell d-orbital electrons of the metal ion they surround. Orbitals that are close to the ligands are raised to slightly higher energy levels and so the five d-orbitals of the 3-d-subshell split into two groups of separate energies. This changes the solution colour because certain wavelengths of light passing through the substance promote the electrons of lower energy d-orbitals to the higher energy d-orbitals. The remaining wavelengths of visible light that are not absorbed during these energy transitions are transmitted and cause the solution's apparent colour.

The complexing agent to be used is ethylenediaminetetraacetic acid (abbreviated to EDTA).



Each EDTA anion acts as a ligand which forms six dative covalent bonds to a Cu²⁺ cation in solution. It is called a hexadentate ligand. An EDTA-copper complex is light-blue in solution. A purple-blue indicator, called murexide, is added before EDTA and in excess to form a complex with the copper(II) ions, colouring the solution a light yellow. During the titration, a ligand substitution reaction occurs because the EDTA²⁻ forms a more stable complex with Cu²⁺. This frees the murexide indicator causing the solution to turn light green near the endpoint and then suddenly purple-blue at the endpoint. Because the molar ratio of reaction 3.0 is 1:1, the concentration of copper(II) of the analyte can be calculated easily from the mean titre of EDTA.

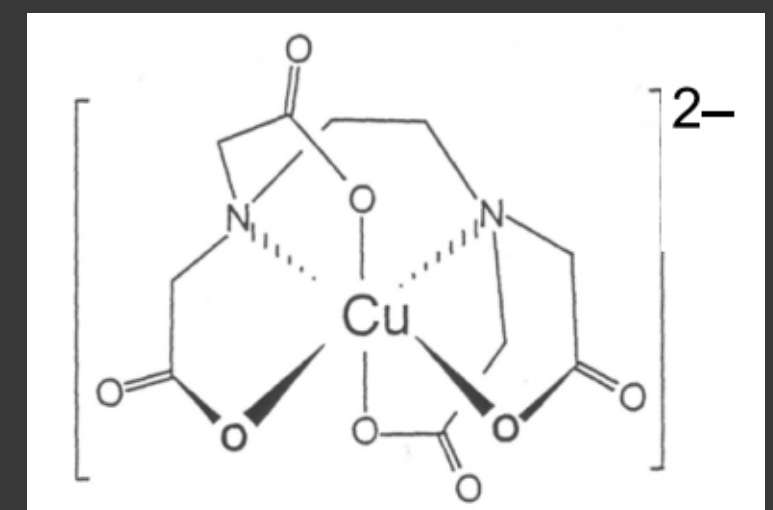


Figure 13.1 Structure of Cu²⁺—EDTA dianion