Electrogravimetric determination of copper

Related concepts
Quantitative analysis, gravimetry, electrolysis, overpotential, electrode polarisation.

Principle
Electrogravimetry is an important analytical method for the quantitative determination or separation of species in solution. The technique involves the quantitative electrolytic deposition of an element, usually a metal, on a suitable electrode in weighable form.

Tasks
Perform an accurate electrogravimetric determination of the amount of copper in a given sample solution.

Equipment
- Power supply, universal 13500.93 1
- Digital multimeter 07134.00 2
- Platinum electrodes for electrogravimetry 45206.00 1
- Connecting cord, \( l = 500 \text{ mm}, \text{red} \) 07361.01 1
- Connecting cord, \( l = 500 \text{ mm}, \text{blue} \) 07361.04 1
- Connecting cord, \( l = 750 \text{ mm}, \text{red} \) 07362.01 2
- Connecting cord, \( l = 750 \text{ mm}, \text{blue} \) 07362.04 1
- Magnetic heating stirrer 35720.93 1
- Magnetic stirrer bar, \( l = 30 \text{ mm} \) 46299.02 1
- Temperature sensor, electronic 35721.00 1
- Support rod, \( l = 500 \text{ mm}, \text{M10 thread} \) 02022.20 1
- Spring balance holder 03065.20 1
- Support rod with hole, \( l = 100 \text{ mm} \) 02036.01 1
- Holder for two electrodes 45284.01 1
- Right angle clamp 37697.00 2
- Analytical balance, with data output, 120 g 48802.93 1
- Beaker, 250 ml, tall 36004.00 3
- Volumetric pipette, 50 ml 36581.00 1
- Graduated pipette, 10 ml 36600.00 1
- Pipettor 36592.00 1
- Pasteur pipettes 36590.00 1
- Rubber bulbs 39275.03 1
- Wash bottle, 500 ml 33931.00 1
- Copper(II) sulphate, 0.1 M, 1000 ml 48247.70 1
- Sulphuric acid, 95…98 %, 500 ml 30219.50 1
- Nitric acid, 65 %, 1000 ml 30213.70 1
- Ethyl alcohol, absolute, 500 ml 30008.50 1
- Water, distilled, 5 l 31246.81 1

Set-up and procedure
Set up the experiment as shown in Fig. 1.
For a quantitative electrogravimetric analysis, the platinum electrodes must be scrupulously clean, and chloride ions should be avoided in all solutions used, since the chlorine that would be produced from them at the anode would attack the platinum.

Fig. 1. Experimental set-up.
Clean the electrodes by dipping them into concentrated nitric acid solution (fume hood), rinsing them thoroughly with distilled water, then drying them, either in an oven at 110°C or by dipping them into pure ethanol and allowing them to air-dry.

Accurately weigh the cylindrical platinum gauze cathode. Clamp the cathode and the spiral platinum wire anode into the electrode holder and fasten it to the support rod of the magnetic stirrer. It may be necessary to bend the anode wire slightly, so that it is positioned centrally within the cylindrical cathode. Lower the electrodes into the 250 ml glass beaker so that the magnetic stirrer bar can still freely rotate. Clamp the thermometer into position between the beaker and the cathode.

Pipette exactly 50 ml of 0.1 M copper sulphate solution and 4 ml of concentrated sulphuric acid solution into the beaker, and add distilled water up to 5-10 mm below the top of the cylindrical wire gauze.

As shown in Fig. 2, connect the multimeter used as ammeter in series, the one used as voltmeter in parallel. Adjust the magnetic stirrer to a medium stirring speed and heat the solution up to a temperature of 70-80°C. Start electrolysis by applying a d.c. potential of +2 V at the anode relative to the cathode.

When the electrolysis current has decreased to approximately one tenth of its initial value (usually after about one hour) the solution should be colourless and electrolysis practically complete. To confirm this, dilute the solution with sufficient distilled water to cover the cathode completely. If, after electrolysis for a further 15 minutes, no fresh copper is deposited on the clean part of the cathode, then, without switching off the voltage supply, remove the thermometer and carefully raise the electrodes. Rinse the electrodes well with distilled water and dry them in an oven or by dipping them into pure ethanol and drying in air. Weigh the platinum gauze cathode again and determine the mass of metallic copper deposited from solution.

**Theory and evaluation**

Electrogravimetry serves predominately for the quantitative determination of cations that, on application of an electric current, are either reduced to metal at a cathode, or oxidized to a sparingly soluble oxide at an anode. The increase in weight at the cathode or anode at the end of electrolysis is determined by weighing, and from this the quantity of cations or anions can be calculated.

Noble metals and Cu, Ni, Co can be particularly well deposited in elementary form. During electrolysis, a cell voltage is required for the continuous deposition of metals at the cathode, or of metal oxides at the anode. The value of this is given by the occurring polarisation voltage (the difference between the anode potential and cathode potential), the concentration polarisation (change in potential due to local depletion of the cations to be determined in the solution), the overvoltage (resulting from reaction inhibitions) and the ohmic resistance of the electrolyte solution.

When a metal is dipped into a solution of a salt, an electrical potential is created at the boundary surface of the phases. Two copper electrodes that dip into the same CuSO₄ solution, both have the same potential. When a very small external current is applied to these electrodes, the equilibrium between Cu²⁺ in the solution and the Cu of the electrodes is disturbed. Copper goes into solution at the anode and an equivalent amount of copper ions are deposited at the cathode. There is therefore no change in the total amount of dissolved copper sulphate. The greater the applied voltage, the quicker this process occurs, and the greater the current. The current-voltage curve increases linearly with increasing voltage. Such attackable electrodes are said to be unpolarizable.
In practice, a more negative potential than that calculated using Nernst's equation is necessary for the deposition of oxygen, i.e. the development of oxygen is inhibited. This difference is called the overvoltage. Overvoltage is dependent on the electrode material, the current density, temperature and the nature of the electrode surface.

The Nernst equation must thus be modified by the overpotential \( \eta \) at the \( \text{H}^+ | \text{O}_2, \text{H}_2\text{O} | \text{Pt} \) electrode:

\[
E_a = E^\phi_{\text{H}^+|\text{O}_2,\text{H}_2\text{O} | \text{Pt}} + \frac{RT}{nF} \ln a_{\text{H}^+} + \eta
\]  

(2)

where

- \( E^\phi_{\text{H}^+|\text{O}_2,\text{H}_2\text{O} | \text{Pt}} \) Anodic potential
- \( E^\phi_{\text{H}^+|\text{O}_2,\text{H}_2\text{O} | \text{Pt}} \) Standard \( \text{H}^+ | \text{O}_2, \text{H}_2\text{O} | \text{Pt} \) half-cell potential (1.23 V)
- \( \eta \) Overpotential

The minimum voltage required to ensure electrolysis \( E_a - E_c \) may be estimated. An initial concentration of copper ions of \( 10^{-1} \) mol / l is assumed and the electrolysis is regarded as being complete when the concentration has fallen to \( 10^{-6} \) mol / l. The pH of the acidic copper sulphate solution is approximately zero and the overpotential is taken to be +0.47 V. Substitution of these values into equations 4 and 5 leads to a minimum calculated voltage range within which quantitative electrolytic deposition of copper at the cathode should occur of 1.39 to 1.54 V. The calculation is approximate since, strictly, overpotentials exist at both electrodes, and are not always simple to quantify exactly, especially in stirred solutions. In addition, the solution between the electrodes represents an ohmic resistance. A certain counter voltage, that is dependent on the type and concentration of the electrolyte as well as on the temperature, must be employed to overcome it.

Electrogravimetry is a very accurate means of quantitatively determining copper, and it should be possible for the student to determine the copper content of the sample solution to an accuracy of 1% or better.
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