Experiment 8: ELECTROGRAVIMETRIC DETERMINATION OF COPPER IN AN ORE

Introduction：

Gravimetric methods of analysis are in general the most accurate of the quantitative methods. This is because mass can be measured with a high degree of precision and accuracy. Most gravimetric analysis requires quantitative transfer and drying of a precipitate. This is a time consuming and error-ridden step in the analysis. In this experiment, gravimetry is combined with electrochemistry to eliminate problems associated with precipitation reaction and quantitative precipitate transfer and preparation. The method used is called *electrogravimetry*. A common example of electrogravimetry is the analysis of copper. Copper is reduced at potentials more positive than the reduction of hydrogen ion, so it can readily be deposited on a platinum cathode from acidic solutions.

In this experiment, the copper ore sample is first oxidized to dissolve all the analyte. Then the analyte solution is *electrolyzed*. When the copper analyte is electrochemically reduced, it deposits out onto the cathode. This process is the basis of metallic electroplating used in manufacturing industries. The cathode (where metal cations will be reduced) has a large area to allow the reduction of solution phase analyte to take place rapidly and quantitatively. The weight of analyte in the ore is determined by weighing the cathode prior to, and after electrolysis.

One problem often encountered in electrodeposition occurs when the cell potential is held constant. Simultaneous reduction of hydrogen ion can occur at low analyte concentrations. In this experiment, concentration of cupric ion is initially high and most all of the cathode current is carried by reduction of cupric ion to copper metal. As the electrolysis proceeds, the concentration of cupric ion falls and the electrode potential becomes increasingly reducing. If no precaution is taken, protons will be reduced and the hydrogen gas liberated and the cathode may cause the copper to flake due to poor adherence to the cathode. This loosely held copper could be lost in handling the electrode. This difficulty is prevented by adding an excess of nitrate ion to the solution. The reduction of nitrate to ammonium ion occurs prior to that of hydrogen thus *buffering* the cathode potential and preventing evolution of hydrogen gas.

Both an anodic and a cathodic reaction must occur for current to pass through the electrolysis cell. In this experiment, the oxidation of water could be the anodic reaction. Greater efficiency is obtained by addition of a small amount of urea. The urea is oxidized at the anode and serves as a *depolarizer*.

The cathode reactions of interest are:

$$Cu^{2+} + 2e^- \rightarrow Cu$$

$$10H^+ + NO_3^- + 8e^- \rightarrow 3H_2O + NH_4^+$$

During electrolysis, formation of nitrite is also possible:

$$2H^+ + NO_3^- + 2e^- \rightarrow H_2O + NO_2^-$$

Nitrite ions prevent complete deposition of copper and are removed by urea:

$$2NO_2^- + 2H^+ + (NH_2)_2CO \rightarrow CO_2 + 2N_2 + 3H_2O$$

Preliminary Calculations：

1. How much copper ore which contains 10% Cu should one take to guarantee that at least 100 mg of Cu will be plated out on the platinum cathode?
2. Assuming a constant current of 1.0 ampere during the electrolysis, how long will it take to plate out 250 mg of Cu?

Procedure：

1. Obtain a copper ore unknown from your instructor. Dry the sample from between 100 ºC and 120 ºC for two hours and cool the dried sample in the desiccator.
2. Weigh copper ore sample accurately (0.1 mg) of about **0.12 g ~ 0.14 g** into the electrolytic beakers. To each sample add **7 mL** of concentrated nitric acid, heat the solutions to just the boiling point until all of the sample has dissolved, then slowly add **70 mL** distilled water. If dissolution is very slow, add additional nitric acid drop-wise until the only residue is white or nearly colorless (if the sample contains silica, it will not dissolve, but removal of all dark material will suffice). Note: care must be taken to avoid loss of sample by spattering!
3. While the samples are being dissolved, prepare the electrodes. Clean them by immersion in concentrated nitric acid. Wash well in distilled water. Dry the cathodes with several small portions of ethanol and dry them in an oven at 100 ºC for several minutes. Cool in a desiccator and weigh each cathode to 0.1 mg.
4. NOTE: the gauze portion of the cathodes should not be touch after cleaning. Dry the cathodes in a clean beaker. Once weighed, they must not be touched with fingers. Handle only with forceps or tissue to prevent grease accumulation.
5. After your unknown solutions have cooled to room temperature, add **0.5 g urea** to each.
6. Ask your Teaching Assistant for details of using the electrolysis apparatus before carrying out the electrolysis. Attach the electrodes to the electrolysis apparatus, cathode to negative terminals, anode to positive terminal. Make sure the two electrodes do not touch !

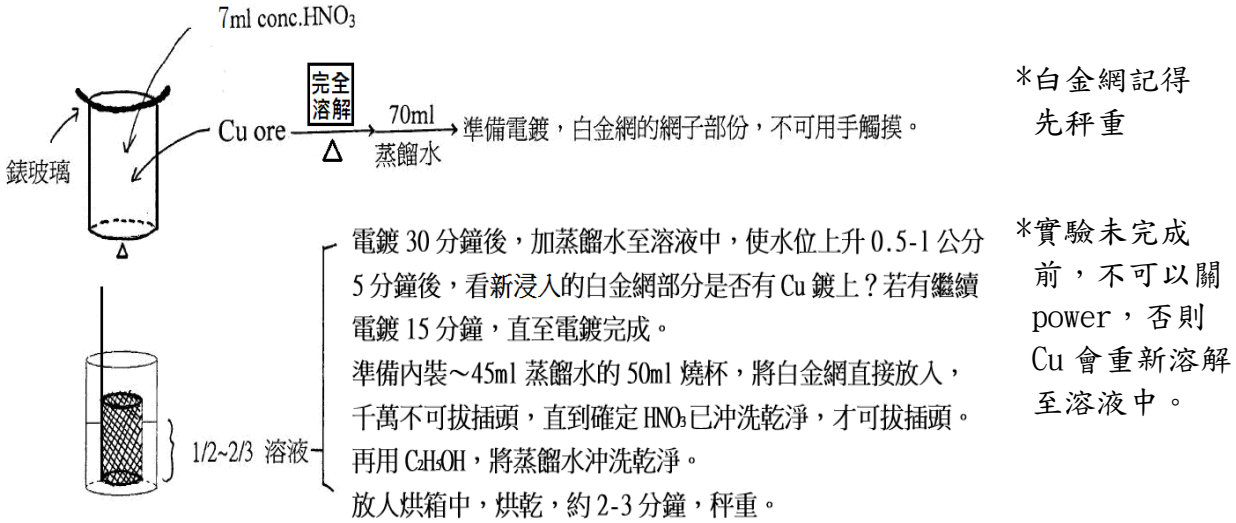
7. Elevate the beaker containing the unknown solutions so that most of the cathode is covered. Leave 1-2 cm uncovered. Start the stirring motor and adjust the applied voltage so that a current of about **1.0** amperes passes through the solution.
8. When the blue color Cu^{2+} has disappeared from the solution (about 30 minutes) add sufficient distilled water to raise the level on the cathode by about 1 cm.
9. If no copper appears on the newly covered portion of the cathode after 15 minutes, the electrolysis is complete. If additional copper does appear, repeat step eight.
10. When no more copper is deposited, slowly lower the beaker while rinsing the electrodes with a stream of water from a wash bottle. **Do not turn off** the applied voltage until the electrodes are completely removed from the solution and rinsing is completed.
11. Disconnect the cathode avoiding finger contact and immerse it in a beaker of distilled water. Then rinse it will several portions of ethanol. Dry the cathodes for **2-3 minutes** at 100 °C, cool in a desiccator, and weigh to 0.1 mg.
12. Clean the cathodes as instructed in step (3) and return them to your instructor.

Questions：

1. Calculate the percent copper in a sample that weighs 2.5003 g and yields 0.1428 g copper upon electrolysis.
2. Write the electrode reactions that occur at the cathode if <u>no nitrate</u> is present.

Results：

Calculate and report weight percent copper in your sample.



儀器設定:

Anode:

Cathode:

結果：

(1) Calculate and report weight percent copper in your sample.

unknown no.	weight of Cu ore(g)	weight of platinum gauze(g)	weight of platinum gauze with Cu(g)	weight percent copper(%)

(2) How much copper ore which contains 10% Cu should one take to guarantee that at least 100 mg of Cu will be plated out on the platinum cathode?

(3) Assuming a constant current of 1.0 ampere during the electrolysis, how long will it take to plate out 250 mg of Cu?

(4) Calculate the percent copper in a sample that weighs 2.5003 g and yields 0.1428 g copper upon electrolysis.

(5) Write the electrode reactions that occur at the cathode if no nitrate is present.