ELECTROGRAVIMETRIC DETERMINATION OF COPPER IN AN ORE

NOTE: You must have your student I.D. card with you the day you perform this experiment in order to check out the (expensive) Pt electrodes.

Background
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, gravimetric analysis is combined with electrochemistry to eliminate problems associated with quantitative precipitate transfer and precipitate 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 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. Adding an excess of nitrate ion to the solution helps prevents this problem. 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 cathode 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:

\[ \text{Cu}^{2+} + 2e^- \rightarrow \text{Cu} \]

\[ 10\text{H}^+ + \text{NO}_3^- + 8e^- \rightarrow 3\text{H}_2\text{O} + \text{NH}_4^+ \]
Metal oxides may be deposited at the anode from a solution with a high nitrate ion concentration. When this happens, the deposition of copper on the cathode may be incomplete. Excess nitrate is removed by the addition of urea:

\[
6\text{NO}_3^- + 6\text{H}^+ + 5(\text{NH}_2\text{C}_2\text{O}) \rightarrow 8\text{N}_2 + 5\text{CO}_2 + 13\text{H}_2\text{O}
\]

**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? answer ____ g

2. Assuming a constant current of 1.0 ampere during the electrolysis, how long will it take to plate out 500 mg of Cu? answer ____ s

**Procedure**

1. Obtain a copper ore unknown from your instructor. Dry the sample from between 100 °C and 120 °C for two hours and cool the dried sample in the desiccator.

2. Turn your student I.D. card into your instructor and in return obtain from a platinum cathode, a platinum anode and two tall-form electrolytic beakers.

3. Accurately (to 0.1 mg) weight out two separate samples of your copper unknown, about 1.0 g each, into the two electrolytic beakers provided. To each sample add 8 mL concentrated Sulfuric (H₂SO₄) and 2 mL concentrated nitric acid (HNO₃) using the acid dispensing pumps in the hood. Then add 40 mL of distilled water several minutes (3-5 minutes) later after most of the sample has dissolved. Heat the solutions to just below the boiling point until the entire sample has dissolved (solution will be blue in color due to the formation of Cu²⁺ ions). If dissolution is very slow, add additional acid (2-3 mL) acid drop-wise until only the insoluble residue remains. Note: care must be taken to avoid loss of sample by spattering! Don’t boil the solution. When the sample has been dissolved, add about 25 mL of 3 M KNO₃ solution and rinse the sides of the beaker with distilled water until the total volume of solution is about 100 mL.

4. While the samples are being dissolved, prepare the electrodes. Clean them by immersion in warm 6 M nitric acid to which 1-2 mL of 3 M KNO₃ have been added. Wash well in distilled water. Rinse the cathodes with several small portions of acetone or ethanol and dry them in an oven at 100 °C for several minutes. Cool and then accurately weigh each cathode to 0.1 mg. **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 (use gloves!).

5. After your unknown solutions have cooled to room temperature, add about 0.5 g of urea to each of the unknown solutions.

6. Check with your lab instructor for details of using the electrolysis apparatus before
carrying out the electrolysis. Attach the electrodes to the electrolysis apparatus, cathode to negative terminals, and 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 2 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. Adjust potential to continue the electrolysis with a current of about 0.5 Ampere.

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 acetone or 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 (4) and return them to your instructor. The limited supply of electrodes makes it imperative that you **DO NOT LOCK THEM IN YOUR DESK.** After returning the electrodes, your student I.D. card will be returned.

**Questions (required, answer these in your lab notebook)**

1. Calculate the percent copper in a sample that weighs 2.3901 g and yields 0.1436 g copper upon electrolysis.

2. Write the electrode reactions that occur at the cathode if no nitrate is present.

3. Write the reaction that will occur at the anode if no urea is present. Why might this reaction not proceed efficiently?

**Results**

Calculate and report weight percent copper in your sample. Grades are based 100% on this value.

**References**