Objective:

In this experiment, gravimetry is combined with electrochemistry to investigate the effects of various factors upon electro-deposition. The method is called Electrogravimetric Analysis.

Theory:

Electrogravimetric analysis is an easy and accurate method for determining metal concentrations using electrochemistry. The element to be determined is deposited as a solid on a pre-weighed electrode throughout a reduction process, and can be measured by the weight gained by the electrode. Selectivity is achieved by using a particular applied voltage that allows only the element to deposit on the electrode. Its main advantages are that filtration is avoided and co-deposition is unlikely when the right conditions are established.

Consider an aqueous solution contacted by two metal electrodes. Application of a sufficiently large DC voltage between the two electrodes will result in a flow of electric charge, i.e. an electrical current.\footnote{Quantitative Chemical Analysis, Daniel C. Harris, 6th ed., Freeman, 2003}

When an electrical current passes a solution, the solution is polarized. In order to understand the implications of polarizing the solution we examine the ways by which electrical charge is carried through the circuit consisting of external voltage source, metal electrodes and solution.

(a) Charge is carried through the external wires and the electrodes by the movement of electrons. This process generally does not result in chemical change.
(b) Charge traverses the polarized solution by the movement of ions. Positive ions or **cations** migrate toward the negative electrode called **cathode**. At the same time, negative ions or **anions** migrate toward the positive electrode called **anode**. The solution remains electrically neutral because the flow of cations and anions is just balanced. Depending on the experimental circumstances, ion conduction may cause a redistribution of materials through a solution but does not generally result directly in chemical transformations.

(c) Charge is transferred across the solution-electrode interface by means of electrochemical reactions at the surface of the electrodes. That is, electrons on the cathode are transferred to some material in the solution, which is said to be **reduced**. Concurrently, an equal number of electrons are transferred to the anode from other material in solution, which is said to be **oxidized**. The solution as a whole remains electrically neutral because equal amounts of charge (electrons) enter the solution at the cathode and leave the solution at the anode. This quantity of charge is called **charge passing the cell** or **charge passing the anode** or **charge passing the cathode**, since all are equal.

By a combination of the three mechanisms above, electrical charge may traverse the entire closed circuit loop consisting of solution, electrodes, and external circuit. It is the last of these mechanisms involving electrochemical reaction, which provides a basis for the following copper analysis.

We now consider a solution of Cu\(^{2+}\) in dilute nitric (HNO\(_3\)) and sulfuric (H\(_2\)SO\(_4\)) acids. Two large electrodes contact the solution and a variable external DC voltage is applied (figure 1). At the beginning a small voltage is applied so that its value is not sufficient to cause the reduction and oxidation processes to occur at the electrodes. As a consequence the electrical current through the solution, electrodes, voltage source circuit is zero. The applied voltage is now increased until its value is high enough to allow electrochemical reduction at the cathode and oxidation at the anode. This minimum applied voltage is termed the **decomposition potential** or **polarization potential of the cell** (combination of solution and electrodes). At applied voltages above the polarization potential, the current-voltage behavior of the cell follows a modified form of Ohm’s Law. That is,

\[
iR = (V - E_d) \quad \text{for} \quad V > E_d
\]

where \(V\) is the applied voltage; \(E_d\) is the polarization potential; \(i\) is the current and \(R\) is the circuit resistance. In other words, the current through the cell remains very close to zero at applied voltages less than \(E_d\) but increases linearly when \(V\) exceeds \(E_d\). A graphical presentation of the cell current \(i\) versus the applied voltage \(V\) is termed the **polarization curve**. The value of the polarization potential is obtained by extrapolating the linear rising portion of the curve to \(i = 0\), then the \(x\)-intercept is \(E_d\).

Suppose now that the applied voltage exceeds \(E_d\) and a current passes the cell. The current is carried through the cell solution by the migration of ions (Cu\(^{2+}\), H\(^+\), NO\(_3^-\), and SO\(_4^{2-}\)). At the anode water is oxidized to oxygen gas according to the half-reaction

\[
2\text{H}_2\text{O} \leftrightarrow \text{O}_2 + 4\text{H}^+ + 4e^-
\]

Electrons on the right-hand-side of the half-reaction represent electrons leaving the solution and entering the platinum electrode. Oxygen formed at the anode surface collects into bubbles and leaves the solution. Several different reduction processes occur at the cathode. At the beginning of the electrolysis the solution is rich in Cu\(^{2+}\) ions that migrate to the cathode fast enough to accept all of the electrons released to the solution. The reduction process at the cathode is

\[
\text{Cu}^{2+} + 2e^- \leftrightarrow \text{Cu}^0
\]

The copper metal formed by this process adheres to the platinum surface. The cathode becomes plated with copper. In effect the passage of current removes Cu\(^{2+}\) from the aqueous solution.
Eventually, the quantity of $\text{Cu}^{2+}$ in solution decreases to such a low level that the migration of copper ions cannot account for all of the electrons supplied by the cathode. At this point, $\text{NO}_3^-$ ions present in the solution are reduced.

$$\text{NO}_3^- + 10\text{H}^+ + 8\text{e}^- \leftrightarrow \text{NH}_4^+ + 3\text{H}_2\text{O} \quad (4)$$

If the electrolysis is allowed to continue for enough time, essentially all of the $\text{Cu}^{2+}$ originally present in the solution is deposited on the cathode. The quantity of copper present in an unknown solution may then be determined by measuring the weight gained by the cathode, i.e. by Electrogravimetry.

NOTE: The nitrate ion in this experiment acts as a "cathode depolarizer". If it were not present, $\text{H}^+$ ions in the solution would be reduced at the cathode and form $\text{H}_2$ gas. This would prevent the element (copper) from adhering properly, resulting in a porous and poorly adherent copper plate. Small pieces would fall off and ruin the analysis.

**Laboratory Procedure**

1. Clean a platinum cathode by dipping it into 6F $\text{HNO}_3$. Thoroughly rinse the electrode with distilled water. Use a strong burner flame to heat the electrode to an orange glow. Cool to room temperature and accurately weigh the electrode. The gauze portion of the electrodes should not be touched with fingers after cleaning to prevent grease accumulation.

NOTE: Electrodes are usually made of platinum, silver or copper. Despite its great expense, platinum is preferred because it is very unreactive and can be heated to very high temperatures to remove volatile organic impurities such as grease that may affect the adhesion of a deposited metal. In addition, large electrodes are preferred, and the main reason is because the best deposits are obtained when the current density is small (less than 0.1A/cm$^2$).

2. Carefully pipet 50 mL of an unknown copper solution into a 200 - 250 mL beaker. Using a graduated cylinder add 2 mL of 6F $\text{HNO}_3$ and 10 mL of 2F $\text{H}_2\text{SO}_4$ to the beaker. Add a stirring bar (stirring almost always improves the quality of the deposit).

3. Set up the electrolysis apparatus: attach the cathode and anode to the negative and positive terminals, respectively. Make sure the electrodes do not touch! Elevate the beaker with the solution so that the cathode is about 2/3 immersed in the copper solution. Add distilled water as necessary.

4. Set the applied voltage control as low as possible. Connect the voltage source and read both the cell current (i) and applied voltage (V). Measure the polarization curve by increasing the applied voltage in steps of 0.1 - 0.2 V, until $V = 2.5$ V. Remember to record both $V$ and $i$. Make these measurements as quickly as possible. Record the time.

5. Read and record the current at 5 - 10 minute intervals. Allow the electrolysis to proceed until the blue solution color has disappeared. When the solution appears colorless add 10-20 ml of distilled water to the beaker and check for further copper deposition after 10 minutes. Continue adding water until no further copper deposit can be detected on the newly covered portion of the cathode.

6. When you have decided that the copper deposition is complete, bring a full wash bottle and two large beakers of fresh distilled water to the workstation. Record the time. Slowly lower the electrolysis solution from the electrodes while these are rinsed with a stream from the wash bottle. Bring a beaker of water up to the electrodes for a further rinse. Do not turn off the applied voltage until the electrodes are completely removed from the solution and rinsing is
completed.

7. Disconnect the cathode avoiding finger contact and immerse it in the second beaker. Finally, rinse the electrodes with methanol. Dry the cathode in an oven (100°C) for 5-10 minutes, cool and weigh to 0.1mg.

8. Clean the cathode by dipping it in a beaker of \( \text{HNO}_3 \). Rinse with distilled water and RETURN THE ELECTRODES TO THE INSTRUCTOR.

**Calculations and discussion**

1. Calculate the concentration of copper in the unknown solution in mol/ L and mg/ mL units.

2. Calculate the error in both copper concentration values. The uncertainty of the balance is ±0.1 mg and of the 50 mL pipet is ±0.08 mL. The graduated cylinders and the beakers are accurate to ±2% and to ±5% of their capacities, respectively.

3. Plot the **polarization curve** (i vs. V) of your electrolysis cell. Extrapolate the rising part of the curve to i = 0 and read the polarization potential \( E_d \). Calculate the slope of the rising portion of the curve. Determine the cell resistance \( R \) from Ohm’s law with its error.

4. Use your current vs. time data to determine the charge (Q = \( \int (i \ast t) \)) that passed the cell. Suppose that \( i = 2.0 \) amps for the first 10 minutes (600 seconds), \( i = 2.2 \) amps for the second ten minutes and remained at 2.4 amps for 20 minutes, when the electrolysis was disconnected. \( Q = 2.0 \times 600 + 2.2 \times 600 + 2.4 \times 1200 = 5.4 \times 10^3 \text{ coulombs} \). NOTE: In this calculation we neglect the small quantity of electricity that passed during the brief period when the polarization curve was measured.

5. (a) What total amount of charge passed the cathode?

   (b) What amount of charge passing the cathode reduced \( \text{Cu}^{2+} \) to copper metal?

   (c) What fraction of the total amount of charge passing the cathode resulted in copper deposition? This fraction, expressed as a percentage, is called the **current efficiency** and is defined as:

   
   \[
   \text{current efficiency} = \frac{Q \text{ (resulting in desired process)}}{Q \text{ (passing the cell)}} = \frac{2 \times \text{moles Cu deposited}}{Q \text{ (passing the cell)}}
   \]

6. (a) What amount of charge passed the anode?

   (b) The formation of \( \text{O}_2 \) (eq. 2) is the only important electrode process at the anode. In other words, the evolution of \( \text{O}_2 \) proceeds with essentially 100% current efficiency under the conditions of this experiment. How many mL of \( \text{O}_2 \) gas at 1.00 atm and 20°C are formed at the anode?

7. (a) Assuming that only \( \text{Cu}^{2+} \) and \( \text{NO}_3^- \) are reduced at the cathode (eqs 3 and 4), what amount of charge (in faradays, \( F = 9.648 \times 10^4 \text{C/mol} \)) was consumed in reducing \( \text{NO}_3^- \) ions?

   (b) How many millimoles of \( \text{NH}_4^+ \) were produced in the solution?

8. Assume that the applied voltage remained constant at 2.5 V and calculate the electrical work done on the electrolysis mixture (electrical work \( W = \int V \ast i \ast dt \), if \( V \) is const \( W = V \times Q \), in joules)