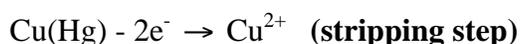
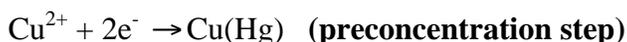


Experiment: Determination of Copper by Anodic Stripping Voltammetry

Principle:

Electrolytic deposition of copper can be performed by preconcentrating Cu from a dilute Cu^{2+} solution, followed by stripping the Cu in the mercury amalgam form (ie. $\text{Cu}(\text{Hg})$) by scanning the electrode potential in the anodic direction. This instrumental analysis technique is referred to as *anodic stripping voltammetry* and it employs 2 steps which can be represented in half reaction form as:



Operating the Controlled Growth Mercury Electrode

Carefully raise the mercury capillary electrode up (**Danger: Do not swing the cell around the capillary and hold the capillary holder loosely, since the breakage of the capillary will result in the spill of toxic Hg!**) by rotating the knob located above the mercury electrode and slide the HMDE upwards. Sliding the cell (glass cup) to the right of the magnetic stirrer and remove it from the set-up (the sliding avoids hitting the capillary tip with the cell). To avoid cross contamination make sure that you have washed the cell, stirring bar, and all electrodes thoroughly before each measurement. Fill the cell with 10 mL of the unknown solution. Place the cell over the magnetic stirrer and switch the stirrer back in position. Bring down the Hg capillary carefully without touching the Teflon holder and position the tip of the capillary below the surface of the solution. Keep the distance of about 0.5 cm-1cm from the bottom of the cell. Adjust the mercury drop by pressing the dispense button located at the top of the instrument. You should see a drop hanging out at the tip of the capillary. Connect the green lead to the working electrode (the lead connecting to the Hg pool), the red lead to the auxiliary electrode (the Pt flag), and the white lead to the reference electrode (the tube-like electrode). Insert the gas purging tube into the sample solution and leave and degas the solution with argon for about 5 minutes. (**Note:** Before you start the analysis, pull the tubing up and leave it above the solution). It is sometimes necessary to ensure good electrical contact between the alligator clips and the electrodes by slightly sanding the points of contact.

Preparation of Unknown Cu solution:

Prepare 500 mL of 0.1 M HNO_3 for later use. (Note that you may need to prepare more of this 0.1 M HNO_3 later if it is not enough). Weigh out accurately 0.5 g of dried Cu ore. (Note: drying to constant weight requires at least 1 hour in the convection oven). Dissolve the Cu ore in 10 mL concentrated HNO_3 in a 250 mL beaker and heat in the hot plate in the hood. (After most of the ore is dissolved you may observe some residue remaining). Cool on the side of the hot plate and add distilled H_2O to the 100-mL mark. Filter this solution using a #42 (or other) filter. Measure filtrate volume with a graduated

cylinder. Prepare a 1:100 dilution and a 1:50 dilution of this filtrate as follows: For the 1:50 dilution, add 2.0 mL of filtrate to a 100-mL volumetric flask and fill to volume with the 0.1 M HNO₃ previously prepared. Prepare the 1:100 dilution solution similarly but using the appropriate filtrate volume. Take these dilutions into account in your final calculation.

Preparation of Standard Cu Solutions:

Ask for 4 mL of 1000 mL Cu²⁺ solution from the instructor or teaching assistant. A micropipet will be used to deliver 4.000mL directly into your 100 mL volumetric flask. Fill to volume with the 0.1 M HNO₃ previously prepared. This is a 40 ppm solution (note: 4 mL (1000 ppm)/(100mL) = 40 ppm). By serial dilution, you are to prepare 50 mL each of the following diluted standards: 20 ppm, 10ppm, 5ppm, 2.5 ppm and 1.25 ppm. For example: to prepare 20 ppm, transfer 50 mL of the 40 ppm standard to a 100-mL volumetric flask and fill to volume with 0.1M HNO₃. That will initially result in 100 mL of 20 ppm (assuming you mix it well). To prepare 10 ppm, transfer 50 mL of your newly prepared 20 ppm to a 100-mL volumetric flask and fill to volume with 0.1 M HNO₃. Continue this process until you have all the standards. Note that you do not need many 100 mL volumetric flasks. Just reuse the volumetric flask and don't use it as your storage container.

Data Collection with the Electrochemical Analyzer

Enter the program by clicking on the **CHI 610a** icon on the **Desktop**. You should take a few minutes to familiarize yourself with the program. Go to **Setup** and click on **Technique**. Scroll down and select **Differential Pulse Voltammetry**. Then go back to setup and click on **Parameters**.

Set the parameters as followed

Int. E(V): enter **0 V**

Fin. E (V): enter **0.35 V**

Sensitivity (A/V): enter **1e-5**

Go to **Control** and scroll down to **Stripping Mode**. Enable the **Stripping mode** and type in 120 s in the deposition panel. Click on the **Run** symbol



and save your spectra after the run is done. Repeat the same for other standards and unknowns.

Unknown Identification

Identify the copper peak present in your voltammogram. Once the identification of your analyte is finished [remember to record peak height (i_p)], ask the teaching assistant for the stock solution for you to prepare the standards. Note: deposition time (120s).

Constructing a calibration curve

After each run record the peak current (i_p) in your notebook (the value will be automatically detected by the program if you choose the "Data Plot" function. To construct your calibration curves plot the peak height (i_p) vs. analyte concentration. Using

the graph of your calibration curve, determine the concentration (ppm) of Cu in your unknown solution.

Standard addition method: Alternatively when the standard addition method is used (valid only under conditions of *linearity* between the i_p and the Cu concentration-which may not be the case for your data), we can use the equation:

$$\frac{i_p'}{i_p} = \frac{[\text{unk}] + [\text{std}]}{[\text{unk}]}$$
 where i_p = peak current signal for unknown alone, i_p' = signal

of the mixture of unknown and added standard

Discarding the waste:

All solutions containing HNO_3 need to be disposed off in the plastic waste bottle labelled “ HNO_3 waste”. **Remember that HNO_3 is a strong oxidant and should not be mixed with other waste which may contain oxidizable material (like alcohol).** Alternatively, the HNO_3 can be rendered neutral by the addition of soda ash until bubbling stops.

References:

1. Lecture textbook: Quantitative Chemical Analysis, Daniel Harris, pages 388-397.
2. Analytical Electrochemistry: Joseph Wang, Call # QD115, W33, 2000.

Informal report

Experiment: Determination of Copper by ASV

Date submitted _____

Time submitted _____

Name _____

Value Obtained: _____ % Cu

Locker # _____

_____ % Cu

Average or best value: _____ % Cu

Standard deviation(if applicable): \pm _____

| Solution (expressed as ppm Cu) | i_p (magnitude in 10^{-6} A) |
|--------------------------------|-------------------------------------|
| 1.25 | |
| 2.5 | |
| 5 | |
| 10 | |
| 20 | |
| Unknown(1:50) | |
| Unknown(1:100) | |

***Attach the standard calibration graph showing all standards and unknown plotted. The y axis is magnitude of i_p (in 10^{-6} A) and x axis is ppm Cu^{2+} . Make sure all axes have linear scales.

***Determine unknown concentration from graph and calculate the % copper as recommended below: (note 1 ppm \approx 1 mg/L)

$$\% \text{Cu} = \frac{(\# \text{ mg/L Cu})(\text{volume (L) of filtrate})(\text{dilution factor}^*)(1\text{g}/10^3\text{mg})(100\%)}{(\text{g ore sample})}$$

* for example: 50 or 100.