

## Experiment: Determination of Copper by Anodic Stripping Voltammetry

### Principle:

Electrolytic deposition of copper can be performed by preconcentrating Cu from a dilute  $\text{Cu}^{2+}$  solution, followed by stripping the Cu in the mercury amalgam form by scanning the electrode potential in the anodic direction. This instrumental analysis technique is referred to as anodic stripping voltammetry.



### 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).

### Preparation of unknown Cu solution:

Prepare 500 mL of 0.1 M  $\text{HNO}_3$  for later use. 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  $\text{HNO}_3$  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  $\text{H}_2\text{O}$  to the 100-mL mark. Filter this solution using a #42 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  $\text{HNO}_3$  previously prepared. Prepare the 1:100 dilution solution similarly but using the appropriate filtrate volume.

### Preparation of standard Cu solutions:

Ask for 4 mL of 1000 mL  $\text{Cu}^{2+}$  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  $\text{HNO}_3$  previously prepared. This is a 40 ppm solution (note:  $4 \text{ mL} (1000 \text{ ppm}) / (100 \text{ mL}) = 40 \text{ ppm}$ ). 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  $\text{HNO}_3$  . 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 HNO<sub>3</sub>. 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 (ppb) of Cd in your unknown solution.

Alternatively when the standard addition method is used ( valid only under conditions of linearity between the  $i_p$  and the Cu concentration), we can use the equation:

$$\frac{i_p'}{i_p} = \frac{[\text{unkn}] + [\text{std}]}{[\text{unk}]} \quad \text{where } i_p = \text{signal for unknown alone,} \\ i_p' = \text{signal of the mixture of unknown and added standard}$$

### Discarding the waste:

All solutions containing HNO<sub>3</sub> need to be disposed off in the plastic waste bottle labelled "HNO<sub>3</sub> waste". **Remember that HNO<sub>3</sub> is a strong oxidant and should not be mixed with other waste which may contain oxidizable material (like alcohol).** Alternatively, the HNO<sub>3</sub> 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**

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  $\text{Cu}^{2+}$ . 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)

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