Introduction:

Cyclic voltammetry (CV) is a widely used electrochemical technique that involves the cyclical scanning of the potential (i.e., scanning from a starting to an ending potential and back again at a constant rate) and measuring the resultant current. The resulting "cyclic voltammogram" relays information about the redox potential of the analyte, the number of electrons transferred in the reduction or oxidation, the reversibility and speed of the electrochemical process, the stability of the oxidized or reduced form of the analyte, and (though rarely used) the concentration of analyte.

In a typical setup, a three electrode cell (working, reference, and counter) is used, with the measured current passing between the working and counter electrodes. The analyte solution must be made to contain a supporting electrolyte, and thus care should be taken to choose an electrolyte that will not react with the analyte or be electroactive within the scan range. Prior to the scan, the solution is degassed with N₂ to remove dissolved O₂. The solution is not stirred during the analysis.

CV is analogous to spectroscopy in that the system is excited by an energy scan, and the response is recorded. A typical excitation signal for CV is a triangular waveform, when plotted as potential versus time (Figure 1). The scan direction may be either in the negative or positive direction, depending on whether a reductive or oxidative process is being studied. Figure 2 shows a typical cyclic voltammogram for a reversible reduction (note that the potential was first swept in the cathodic direction, resulting in a positive current, and then in the anodic direction, resulting in a negative peak with approximately the same area). The important parameters of a cyclic voltammogram are the magnitudes of the anodic and cathodic peak currents (iₚₐ and iₚₖ respectively) and of the anodic and cathodic peak potentials (Eₚₐ and Eₚₖ respectively), which are labeled in Figure 2 (note the extrapolations of the baselines to determine the peak currents).

An "electrochemically reversible couple" refers to a redox process in which both the oxidized and reduced form of the analyte rapidly exchange electrons at the electrode. The cyclic voltammogram in Figure 2 shows the result of a CV analysis of such a species, wherein the cathodic and anodic peaks are

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**Figure 1: Excitation Signal for CV**

**Figure 2: Typical CV showing a reversible reduction**

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symmetric, but occur at slightly offset potentials. (Semi-reversible couples occur when the rates of
 electron exchange for the oxidized and reduced species are substantially different, such as may happen
 if one of them is a solid or a liquid; irreversible couples occur when the species decomposes after
 electron exchange, and therefore is not available for the reverse electron exchange). For reversible
couples, the formal reduction potential is centered between $E_{pa}$ and $E_{pc}$, found mathematically by:

$$E = \frac{E_{pa} + E_{pc}}{2}$$

the number of electrons transferred in the reaction at the electrode is given by:

$$\Delta E = |E_{pa} - E_{pc}| \approx \frac{0.059}{n}$$

and the ratio of the peak currents is unity:

$$\frac{i_{pa}}{i_{pc}} \approx 1$$

Finally, the peak current is given by:

$$i_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} C \nu^{1/2}$$

where $n$ is the number of electrons, $A$ is electrode area, $D$ is the diffusion coefficient, $C$ is the
concentration, and $\nu$ is the scan rate (e.g. V/s). Thus, a great deal of information can be learned about
the system by varying known parameters, such as concentration and scan rate.

In this lab, you will be given a compound known to undergo a reversible redox couple. You will
begin by sweeping through the usable range of potentials, as governed by the instrumental setup (in this
case, the working electrode will be mercury) to find the approximate redox potential of the analyte.
You will then perform a series of cyclic voltammetry analyses, varying the scan rate and concentration,
so determine the effects of these parameter changes on the analysis.

**Equipment:** Read through the procedures and make a list of the equipment you will need.

**Safety Considerations:** Read through the procedures and note any safety considerations.

**Procedure:**

**A. Solution preparation**

1. You will be supplied with an Electrolyte Solution (0.05M NaClO$_4$ / 0.01 M H$_2$SO$_4$) and a Stock
Solutions (50.0 mM Cd(NO$_3$)$_2$ in Electrolyte). Use these solutions to prepare 50 mL each of 0.2,
0.5, 1.0 and 2.0 mM solutions of Cd(NO$_3$)$_2$. Dilute each solution using Electrolyte Solution, *not
water!*

**B. Electrochemical Analysis**

1. Wipe the Pt counter electrode to ensure it is clean.
2. Fill the Ag/AgCl reference electrode with filling solution (AgCl$_2$ saturated KCl) and assemble.
3. Place a sample of 0.5 mM Cd(NO$_3$)$_2$ in the cell and purge for one minute with N$_2$.
4. The working range of a mercury electrode is roughly 0.25 V to -1.1 V. The redox couple for Cd
is in a much narrower range. Set up a CV to scan 0.0 to -0.7V at 100 mV/s.
5. After waiting a few minutes for the solution to settle, run the scan.
6. Set up and perform scans on this 0.5 mM Cd(NO$_3$)$_2$ at scan rates of 20, 50, 100, and 200 mV/s.
Between scans, stir the solution very briefly and allow a minute or two for the system to come
to rest.
7. Set up and perform a series of scans on the remaining solutions (0.2, 1.0 and 2.0 mM solutions
of Cd(NO$_3$)$_2$) using the same scan range as in Step B4 and a scan rate of 50 mV/s
8. Export all the data, save on a USB drive.
Analysis (Lab Notebook)
The following must be completed in your lab notebook before you can turn in your Notebook Report:

1. Using Excel or another spreadsheet program make two plots of the data (i vs E):
   a) In one plot, place the 8 scans of the 0.5 mM solution at different scan rates.
   b) In a second plot, place the 4 scans of different concentrations at 50 mV/s scan rate
   c) Print these plots and put them in your notebook
2. From your plots of i vs E, determine \( i_{pa} \), \( i_{pc} \), \( E_{pa} \) and \( E_{pc} \) for each scan. Record these in a table (you may wish to do this in Excel for ease of calculations and print out the final tables).
3. Calculate \( \Delta E \) for each of scans. Comment on any trends in scan rates or concentration.
4. Calculate n for each of scans. Comment on any trends in scan rates or concentration.
5. Calculate \( E \) for each of scans. Comment on any trends in scan rates or concentration.
6. Calculate \( i_{pa} / i_{pc} \) for each of the scans using the same sample (0.5mM) but different scan rates (Step B6). Comment on any trend.
7. Comment on any trend between concentration and current (\( i_{pa} \)).

Lab Report including Conclusions and Discussion
Your lab report is due by lecture on Wednesday, . Your report must be handed in BOTH electronically (via Moodle) and in hard copy form. See the document "LabReportGuide.pdf" on the course website (http://oz.plymouth.edu/~jsduncan/courses/2013_Fall/InstrumentalAnalysis) for guidelines on writing your report.

1. Determine the effect of scan rate on peak height by plotting the anodic peak current versus square root of scan rate (\( i_{pa} \) vs \( \sqrt{v} \)).
2. Determine the effect of scan rate on \( \Delta E \) by plotting \( \Delta E \) vs v using the scans of the same sample but different scan rates (Step B6).
3. Determine the effect of concentration on peak current by plotting \( i_{pa} \) versus concentration of analyte from the scans of various analyte concentrations but same scan rate.
4. What would a cyclic voltammogram look like if the solution were stirred constantly through the analysis?