Brooklyn College
Department of Chemistry

Instrumental Analysis (CHEM 42/790G) Voltammetry

I. Cyclic Voltammetry

This experiment illustrates the use of cyclic voltammetry to study a redox reaction. The Bioanalytical Systems CV-27 Voltammograph is used to study the redox couple ferrocyanide/ferricyanide in aqueous solution using a platinum electrode.

Experimental Procedure

Solutions

Supporting electrolyte stock solution. Prepare 250 mL of 0.2 M KNO_3 solution.

Iron Complex Standards. Prepare a 100 mL stock solution of 10 mM $K_4Fe(CN)_6$ x 3 H_2O (422.4 g/mol) in 0.2 M KNO_3 (use an analytical balance to weigh $K_4Fe(CN)_6$, dilute to the mark with 0.2 M KNO_3 solution). Serial dilutions of this solution with the supporting electrolyte stock solution are performed to give 25 mL solutions of 1, 2, 4 and 6 mM $K_4Fe(CN)_6$ x 3 H_2O in 0.2 M KNO_3.

Unknown. The unknown will be provided in a 25 mL volumetric flask. Dilute to the mark using the 0.2 M KNO_3 stock solution.

Front Panel Set-up

A. Turn the Cell Mode switch to the STBY position.

B. Turn the POWER switch on.

C. Turn the DISPLAY knob to App E.

D. Turn the FUNCTION knob to E1 and ajust the INITIAL E, E1 knob until the number in the display window shows -0.20 V.

E. The procedure used for setting E1 is summarized below. Follow the same procedure to adjust the other experimental parameters shown:

Turn Display:	Use this Control	to set this value:
App E	FUNCTION knob to E1	
	INITIAL E, E1 to	-0.20 V
+Lim	E LIMIT, + knob to	+0.80 V
-Lim	E LIM, -knob to	-0.20 V
Scan Rate	SCAN V/s rotary switch to	0.10
	SCAN RATE knob to	50 mV/s

F. Turn the DISPLAY knob counterclockwise to the App E position.

G. Push the DIRECTION toggle switch upward for positive scan.

H. Set the GAIN switch to the 0.020 mA/V position.

Cell Set-up

A. Place the sample solution (6 mM $K_4Fe(CN)_6$ in 0.2 M KNO_3) in the glass cell in the Cell Stand.

B. Place the Ag/AgCl reference electrode, the platinum working electrode, and the platinum auxiliary (counter) electrode through the cell top and into the solution. Polish the working electrode before each scan.

C. Connect the electrode leads: WHITE to reference; RED to auxiliary; BLACK to working.

The Experiment

A. Turn X-Y recorder On, Pen Up, and zero the X and Y axes somewhere near the center of the paper. Set the X and Y axis ranges to 0.1 V/division (adjust as needed to get a reasonable display).

B. Turn the FUNCTION knob to the HOLD position.

C. Turn the CELL MODE knob to the CELL position (the recorder pen will jump to the initial potential selected on the X-axis and there will be a momentary current pulse).

D. Put the recorder Pen down.

E. Turn the FUNCTION knob to the SCAN position.

NOTE: The recorder pen will move to the left (increasing positive potential) at the scan rate of 50 mV/s. Anodic current corresponding to the oxidation of iron(II) will be observed. The potential scan will reach its positive limit of +0.80 V and the reverse scan towards –0.20 V will begin. Cathodic current due to the reduction of the iron(III) (generating during the initial scan) will be observed during the reverse scan.

F. At the completion of the reverse scan, lift the pen on the recorder and turn the FUNCTION knob to HOLD to stop the experiment.

G. Repeat the experiment for 1, 2, 4 mM standard solutions and the unknown solution. Polish the working electrode before each scan. Run 2 mM standard solution as the last one.

H. Run the experiment for 2 mM standard solution at scan rates of 5, 10, 20, 50 and 100 mV/s. Polish the working electrode before each scan.

Data Analysis

A. Measure the oxidation peak current for each concentration of $Fe(CN)_6^{4-}$ and the unknown. This can be measured with respect to the Y=0 axis or the baseline current at the appropriate potential as measured above. The current is obtained by multiplying the peak height (cm) times the recorder Y-axis sensitivity (V/cm) times the instrument gain (mA/V). Tabulate and plot this data on a spreadsheet. Report the concentration (mM) of $K_4Fe(CN)_6$ in the unknown.

A. For 2 mM $Fe(CN)_6^{4-}$ calculate and tabulate the electrochemical data listed below.
v (mV/s); i_p^a (μA); i_p^c (μA); E_p^a (V); E_p^c (V)

B. Compare your experimental results with the following theoretical results for a diffusion-controlled, reversible electrode reaction:
Anodic and cathodic peak currents are approximately the same.
The difference in peak potentials is approximately 0.059/n (V), where n is the number of electrons involved in the half reaction.
The potential midway between the two peak potentials is the formal electrode potential (corrected for the reference electrode being used) for the redox couple.
The peak current for the forward sweep of the first cycle is proportional to the square root of the scan rate.

II. Stripping Voltammetry

Anodic Stripping Voltammetry (ASV) is used in this experiment for the determination of Pb^{2+}. ASV is commonly used for the determination of metal ions at the trace level because of its excellent detection limit (typically 10^{-9} - 10^{-12} M). During the first phase of a determination, the analyte is deposited (reduced to its elemental form) at the electrode by controlled potential electrolysis in a stirred solution. In the second phase, the stirring is turn off and the potential of the electrode is scanned so that the deposited metal is oxidized back to its ionic form, i.e. anodically stripped from the electrode.

Materials

A solution of the unknown (Pb^{2+}) in 0.1 mM Hg^{2+} / 0.1 M KNO_3 is provided.
A 25 ppm Pb^{2+} stock solution is provided.
The concentration of Pb^{2+} in the unknown will be determined by two additions of the standard Pb^{2+} solution.
The glassy carbon working electrode, the Ag/AgCl reference electrode, and the platinum auxiliary electrode are used in this experiment.
The working electrode must be polished before each voltammetric scan.

Experimental Procedure

Instrument Set-Up

Follow the same procedure used in the CV experiment to adjust these experimental parameters:

Turn Display:	Use this Control	to set this value:
App E	FUNCTION knob to E1	
	INITIAL E, E1 to	-1.00 V
	FUNCTION knob to E2	
	INITIAL E, E2 to	+1.00 V
+Lim	E LIMIT, + knob to	–0.10 V
-Lim	E LIM, -knob to	–1.00 V
Scan Rate	SCAN V/s rotary switch to	0.1
	SCAN RATE knob to	40 mV/s

Turn the GAIN switch to the 0.020 mA/V setting.
Place 8 mL of the unknown Pb^{2+} solution and a stirring bar in the glass cell (be very careful with a stirring bar it is very small, DO NOT LOSE IT).
Add the electrodes and connect the electrode leads as before: WHITE to reference; RED to auxiliary; BLACK to working.

Insert the appropriate larger gas tube into the solution and the smaller one above the surface of the sample. Degas the solution for 10 minutes using the controls on the C-1B Cell Stand.

Stop degassing. Turn on the magnetic stirrer. The stirring speed must be constant throughout all experiments.

Turn the CELL MODE knob to the CELL position and start the timer.

Use a deposition time of 120 seconds (the deposition potential, E1, is –1.00 V. At this time, stop the stirring and wait for the solution to become stationary. Use 30 seconds for this quite time (–1.00 V, no stirring). During those 30 s, turn the FUNCTION knob to the HOLD position and put down the recorder pen. Both times (210 and 30 s) must be constant throughout all experiments.

At the end of the quiet time, turn the FUNCTION knob to the SCAN position.

NOTE: The recorder pen will slowly move to the left (increasing positive potential) at the scan rate of 40 mV/s. A stripping peak will appear at approximately –0.45 V vs. Ag/AgCl.

At the end of each potential scan, lift the pen on the recorder, turn on the magnetic stirrer and **switch the FUNCTION**