Brooklyn College
Department of Chemistry

Chemistry 41 ***Voltammetry***

This experiment illustrates the use of voltammetry to study a redox reaction. The Bioanalytical Systems CV-27 Voltammograph is used to study the oxidation of the hexacyanoferrate(II) ion:

$Fe(CN)_6^{4-} \rightarrow Fe(CN)_6^{3-} + e^-$

Voltammetry is discussed in Chapter 21 of your text. In particular, Section 21B-3 describes the appearance of a typical voltammogram.

The electrochemical cell is a three-electrode system. The working electrode (platinum disk electrode) is the one at which the reaction to be studied occurs. Its potential is measured with respect to a reference electrode (silver/silver chloride). The third electrode (platinum wire electrode) is called the auxiliary (or counter) electrode; current flows between the working and auxiliary electrodes.

The solution to be analyzed contains $Fe(CN)_6^{4-}$ ions in the presence of a supporting electrolyte of potassium nitrate. The CV-27 is set-up to linearly sweep the potential of the working electrode from –0.1 V to +0.9 V. At a potential of about +0.4 V the hexacyanoferrate(II) ion begins to be oxidized to the hexacyanoferrate(III) ion and the resulting current flow is plotted. Eventually the rate at which the reactant can be brought to the surface of the electrode by mass-transport processes limits the flow of current. Under hydrodynamic conditions, as with stirring or with a rotating electrode, a current plateau is reached (see Fig. 21-7 in text). However, we use an unstirred solution, and diffusion is the only process to bring iron(II) complex from the bulk solution to the electrode where the concentration of this complex is practically zero (when the oxidation process occurs). Hence the voltammograms obtained in our experiment show a current peak followed by a current that declines rapidly. The peak current is proportional to the concentration of hexacyanoferrate(II) ion, and a calibration curve of peak current versus hexacyanoferrate(II) ion concentration is used to analyze an unknown.

Experimental Procedure

Preparation of Solutions.

Supporting electrolyte stock solution. Dissolve approximately 50 g of KNO_3 (101 g/mole) in 500 mL of water to give a 1.0 M solution.

Iron Standards. Prepare a 100 mL stock solution of 10 mM $K_4Fe(CN)_6$ x 3 H_2O (422.4 g/mol) in 1.0 M KNO_3. Accurately weigh about 420 mg of the iron salt for this solution. Do NOT dry the salt since it is hydrate. Serial dilutions of this solution with the supporting electrolyte stock

solution are performed to give 25 mL solutions of 2, 4, 6 and 8 mM $K_4Fe(CN)_6$ x 3 H_2O in 1.0 M KNO_3.

Unknown. The unknown will be provided in a 100 mL volumetric flask. Dilute to the mark using the 1.0 M KNO_3 stock solution.

Procedure.

Front Panel Set-up

A. Turn the CELL MODE switch to the STBY position **(if you are not running measurements this switch MUST be in STBY position)**.
B. Turn the POWER switch on.
C. Turn the DISPLAY knob to App E.
D. Turn the FUNCTION knob to E1 and adjust the INITIAL E, E1 knob (the smaller knob) until the number in the display window shows –0.10 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	–0.10 V
+Lim	E LIMIT, + knob to	+0.90 V
-Lim	E LIM, -knob to	–0.10 V
Scan Rate	SCAN V/s rotary switch to	0.10
	SCAN RATE knob to	20 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 0.050 mA/V position.

Cell Set-up

A. Place the sample solution in the glass cell (always rinse the cell with the solution to be analyzed before filling it) in the Cell Stand.
B. Place the Ag/AgCl reference electrode, the glassy carbon working electrode, and the platinum auxiliary (counter) electrode through the cell top and into the solution. **Handle the electrodes with care.**
C. Connect the electrode leads: WHITE to reference; RED to auxiliary; BLACK to working.

Recorder Set-up

A. Turn X-Y recorder On. Pen switch Up. Load paper. Paper switch DOWN. Standby/Measure switch to MEASURE. **(Caution! The recorder arm moves very fast!)**

B. Set the X-axis sensitivity to 0.05 V/cm, calibrated. Set the Y-axis ranges to 0.05 V/cm, calibrated.

C. Use the ↔ knobs to zero the X and Y axes somewhere near the upper right-hand corner of the chart. (Approximately X=25 and Y=18 using the scales on the recorder.)

The Experiment

A. Turn the FUNCTION knob to the HOLD position.

B. 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).

C. Put the recorder Pen down.

D. 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 20 mV/s. Anodic current corresponding to the oxidation of iron(II) will be observed. The potential scan will reach its positive limit of +0.90 V and the reverse scan towards -0.10 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.

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

F. Then turn the FUNCTION to E1 to reset the potential to –0.1 V.
You may observe positive current (reducing current) as the Fe(III) accumulated at the electrode is reduced back to Fe(II). If you want to repeat a scan, gently move the working electrode up and down several times to bring fresh solution o the surface.

G. Turn the CELL MODE knob to STANDBY. Do this any time you are changing solutions or removing any of electrodes.

H. Repeat the procedure above for the other standard solutions and for the unknown. Rinse the electrodes with deionized water and lightly polish the working electrode with a Kim-Wipe when changing samples. Change the recorder Y-axis sensitivity or the instrument gain with the dilute solutions in order to minimize the error in measuring the peak heights.

I. Repeat the procedure for the supporting electrolyte alone. Use this scan to determine a baseline current and to check for oxidizable impurities.

Data Analysis and Report

Measure the peak current for each voltammogram. 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. Determine a least squares fir to your data. Submit the spreadsheet for your report. Report the concentration (mM) of $K_4Fe(CN)_6$ in the unknown.