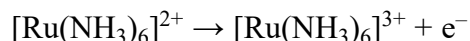


Using RuHex in Quantitative Cyclic Voltammetry

Cyclic voltammetry (CV) is a very versatile and important electroanalytical technique for studying electroactive chemicals. During a CV experiment, the potential at the working electrode is controlled versus a reference electrode (in the screen-printed electrodes you will use in this experiment, it is Ag/AgCl). The controlling potential that is applied is the excitation signal. This excitation varies linearly with time. It can be first applied positively (for example, $-100 \text{ mV vs. Ag/AgCl}$ to $500 \text{ mV vs. Ag/AgCl}$). Then it can be applied negatively as you scan back to the original potential to complete two segments. The process can be done multiple times on the same surface. A cyclic voltammogram is the plot of the response current at the working electrode to the applied excitation potential. These voltammograms can be analyzed for fundamental information regarding the redox reaction that you are monitoring. They are the electrochemical equivalent to the spectra obtained in optical spectroscopy. Just like spectra, these voltammograms have the potential to yield qualitative, quantitative, thermodynamic, and kinetic information about redox active species.

To use cyclic voltammetry effectively, you need to know how to assess your voltammograms and change operational parameters, such as potential limits and sweep rate, to optimize the data. In this experiment you will observe how changes in the instrument's settings alter voltammograms of a redox reaction using the redox couple ruthenium hexamine (RuHex):



You will also explore fundamental aspects of a voltammogram and what information voltammograms can yield to help you learn about a redox system.

A redox couple in which half reactions rapidly exchange electrons at the working electrode are said to be electrochemically reversible couples. The formal reduction potential (E^0) for such a reversible couple is the mean of anodic peak potential (E_{pa}) and cathodic peak potential (E_{pc}) when the anodic peak current (i_{pa}) and the cathodic peak current (i_{pc}) are close in magnitude.

$$E^0 = (E_{pa} + E_{pc}) / 2$$

Through the Nernst equation, we can relate the number of electrons (n) involved in a redox reaction for a reversible process to the peak potentials:

$$E_{pa} - E_{pc} = 59 \text{ mV}/n$$

For slow electron transfers at the electrode surface (i.e., electrochemically irreversible processes), the difference between the peaks widens. The peak current is given by the Randles-Sevcik equation:

$$i_{pc} = 2.69 \times 10^8 \text{ n}^{3/2} A D^{1/2} \nu^{1/2} C$$

where i_{pc} = peak current in A, n = number of electrons, A = electrode area in m^2 , D = diffusion coefficient in m^2/s , C = concentration in mol/L , and ν = sweep rate in V/s . The importance of this nomenclature will become more apparent as you investigate your voltammograms.

OBJECTIVES

- Use an electrochemical technique called cyclic voltammetry.
- Explore how changes in the current, potential, and sweep rate affect a voltammogram.
- Make a standard curve using cyclic voltammetry and then use the curve to determine the concentration of an unknown sample.
- Optimize a voltammogram for RuHex.
- Determine if the reaction is a reversible redox couple or irreversible.
- Explore the relationship between sweep rate and peak current.

MATERIALS

One of the following

- Chromebook, computer, or mobile device with Vernier Instrumental Analysis app¹
- LabQuest 2 (software is pre-installed; v2.8.7 or newer required)²
- LabQuest 3 (software is pre-installed; v3.0.6 or newer required)²

Go Direct Cyclic Voltammetry System and stand

screen-printed electrode (SPE)

scintillation vials

6.0 mM hexaammineruthenium stock solution in 0.1 M potassium chloride

0.1 M potassium chloride solution

RuHex sample of unknown concentration

goggles

Graphical Analysis app (used for data analysis)³

PRE-LAB ACTIVITY

Calculate and describe how you would accurately prepare 10 mL each of the following solutions from your 6.0 mM RuHex stock solution: 3.0 mM, 1.2 mM, 0.6 mM, and 0.0 mM. Note the solvent you will use for dilution.

PROCEDURE

Part I Solution preparation

1. Put on safety goggles.
2. Based on your pre-lab calculations, accurately prepare 25 mL each of the following solutions from your 6.0 mM RuHex stock solution: 3.0 mM, 1.2 mM, 0.6 mM, and 0.0 mM. Dilute with 0.1 M potassium chloride. **WARNING:** *Hexaammineruthenium(III) chloride, $\text{H}_{18}\text{Cl}_3\text{N}_6\text{Ru}$: Causes skin irritation, causes serious eye irritation, may cause respiratory irritation.*

¹ Instrumental Analysis v1.2 or newer required; download the most recent version for free at www.vernier.com/ia

² Download the most recent version of LabQuest software for free at www.vernier.com/downloads

³ Vernier Graphical Analysis app is available as a free download at www.vernier.com/ga

Part II Voltammogram of RuHex solution

- Set up the Cyclic Voltammetry System by following the directions for your equipment:

Instrumental Analysis

- Launch Instrumental Analysis.
- Connect the Go Direct Cyclic Voltammetry System (CVS) to your device via USB or Bluetooth wireless technology. If using Bluetooth, click or tap Connect an Instrument, connect to your CVS, and click or tap Done.
- Click or tap Voltammetry.
- Set the CV Profile settings to the values in Table 1.

LabQuest

- Connect the Go Direct Cyclic Voltammetry System (CVS) to your device via USB or Bluetooth wireless technology. If using Bluetooth, tap the Sensors menu and choose Wireless Device Setup ► Go Direct. Select your instrument and tap OK.
- Choose Data Collection from the Sensors menu.
- Set the CV Profile settings to the values in Table 1. Make sure the Voltammetry mode is set to Cyclic Voltammetry.

Table 1	
Number of segments	3
Initial potential (mV)	0
Switching potential 1 (mV)	500
Switching potential 2 (mV)	−1500
Final potential (mV)	0
Sweep rate (mV/s)	100
Current range	High ($\pm 1000 \mu\text{A}$)

- Insert a screen-printed electrode (SPE) into the SPE connector on the Cyclic Voltammetry System (see Figure 1).

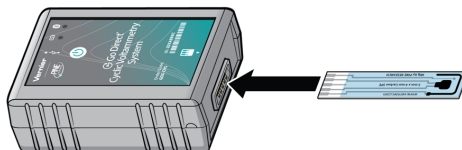


Figure 1

Experiment 4

5. Obtain a background voltammogram.
 - a. Fill the scintillation vial about halfway full (~10 mL) with your 0.1 M potassium chloride solution. Insert the scintillation vial into the clip on the stand. Carefully guide the Cyclic Voltammetry System with SPE attached downward into the vial and snap the instrument into place, as shown in Figure 2. **Caution:** *Treat all laboratory chemicals with caution. Prudent laboratory practices should be observed.*
 - b. Start data collection. When data collection is complete, examine the background cyclic voltammogram. The voltammogram should exhibit no significant peaks (other than random sub-microampere noise). The overall background current should be less than 500 nA. If significant peaks are apparent, then the buffer, the glassware, and/or the electrode surface are likely contaminated. Consult your instructor if excessive or unusual background current is observed.
 - c. Name your sample appropriately.

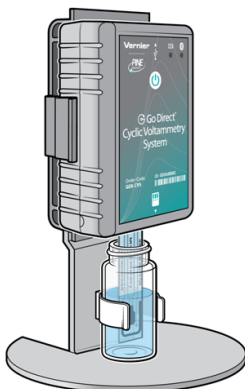


Figure 2

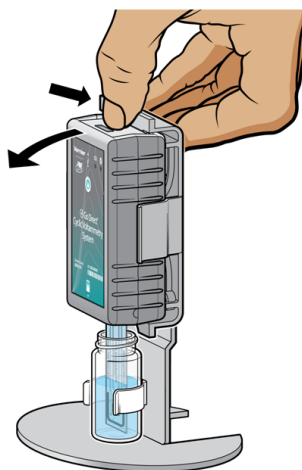


Figure 3

6. Obtain a voltammogram of your RuHex solution.
 - a. Carefully remove the Cyclic Voltammetry System from the holder by pulling back on the top tab (see Figure 3).
 - b. With the SPE still inserted in the Cyclic Voltammetry System, rinse the SPE with buffer solution, and dry it by gently blotting the electrode surface with a piece of paper towel. **Important:** Do not invert the Cyclic Voltammetry System with a damp SPE attached. You want to avoid getting liquid inside the SPE connector.
 - c. Discard the potassium chloride solution from the scintillation vial. Fill it half way full with the 6.0 mM RuHex solution. Replace the vial in the holder. Replace the Cyclic Voltammetry System with the SPE attached in the holder. **Caution:** *Treat all laboratory chemicals with caution. Prudent laboratory practices should be observed.*
 - d. Start data collection. When data collection is complete, name your sample appropriately.
 - e. In Table 7, record your observations of the voltammogram, identify the anodic and cathodic peaks in the voltammogram, and sketch a drawing of voltage vs. time that adequately portrays the parameters set.

7. Adjust the number of segments and the potentials, and repeat the voltammogram of RuHex.
 a. To adjust the settings, follow the directions for your equipment:

- Instrumental Analysis: Click or tap Voltammetry Settings, $\overline{\infty}$. Set the parameters to the values in Table 2.
- LabQuest: Choose Data Collection from the Sensors menu. Set the CV Profile settings to the values in Table 2.

Table 2	
Number of segments	2
Initial potential (mV)	200
Switching potential 1 (mV)	-700
Switching potential 2 (mV)	200
Final potential (mV)	100
Sweep rate (mV/s)	High ($\pm 1000 \mu\text{A}$)

- b. Start data collection. When data collection is complete, name your sample appropriately.
- c. In Table 7, record your observations of the voltammogram, particularly as they apply to variation from the previous voltammogram, and sketch a drawing of voltage *vs.* time that adequately portrays the parameters set.
8. Adjust the sweep rate and repeat the voltammogram of RuHex.
 a. Set the voltammetry parameters to the values in Table 3.

Table 3	
Number of segments	2
Initial potential (mV)	200
Switching potential 1 (mV)	-700
Final potential (mV)	200
Sweep rate (mV/s)	25
Current range	High ($\pm 1000 \mu\text{A}$)

- b. Start data collection. When data collection is complete, name your sample appropriately.
- c. In Table 7, record your observations of the voltammogram, particularly as they apply to variation from the previous voltammogram, and sketch a drawing of voltage *vs.* time that adequately portrays the parameters set.

Experiment 4

9. Adjust the current range and repeat the voltammogram of RuHex.
 - a. Set the voltammetry parameters to the values in Table 4.


Table 4	
Number of segments	2
Initial potential (mV)	200
Switching potential 1 (mV)	-700
Final potential (mV)	200
Sweep rate (mV/s)	25
Current range	Medium ($\pm 100 \mu\text{A}$)

- b. Start data collection. When data collection is complete, name your sample appropriately.
 - c. In Table 7, record your observations of the voltammogram, particularly as they apply to variation from the previous voltammogram, and sketch a drawing of voltage vs. time that adequately portrays the parameters set.
10. With the knowledge you have from the previous steps, adjust any of the values to obtain the optimal voltammogram. Add any additional parameter changes to Table 7 and record your observations. Record your final optimized parameters in this table as well.

Part III Voltammograms at various sweep rates

11. Obtain voltammograms of RuHex at various sweep rates.
 - a. Set the voltammetry parameters to the values in Table 5.

Table 5	
Number of segments	2
Initial potential (mV)	200
Switching potential 1 (mV)	-700
Final potential (mV)	200
Sweep rate (mV/s)	25
Current range	Medium ($\pm 100 \mu\text{A}$)

- b. Start data collection. When data collection is complete, name your sample appropriately.
 - c. With the knowledge you have from the previous steps, adjust any of the values to obtain the optimal voltammogram. Record your final optimized parameters.
 - d. Analyze the voltammogram to obtain the anodic and cathodic peak currents (μA).
 - Instrumental Analysis: Click or tap Graph Tools, , and choose View Statistics. Record the anodic and cathodic peak currents (μA) in Table 8.
 - LabQuest: Choose Statistics from the Analyze menu. Record the anodic and cathodic peak currents (μA) in Table 8.

- e. Repeat Steps a–d for the following additional sweep rates: 50 mV/s, 100 mV/s, 200 mV/s, 300 mV/s, 400 mV/s, and 500 mV/s. **Note:** Apply the skills you learned in the previous part to optimize your voltammograms.
12. Carefully remove the Cyclic Voltammetry System from the stand by pulling back on the top tab. With the SPE still inserted, rinse the SPE with potassium chloride solution, and dry it by gently blotting the electrode surface with a lint-free wipe or piece of paper towel.
Important: Do not invert the Cyclic Voltammetry System with a damp SPE attached. You want to avoid getting liquid inside the SPE connector.
13. Set aside the 6.0 mM solution in the scintillation vial; you will test it again later.

Part IV Voltammograms at various concentrations, identifying an unknown solution

14. Fill another vial approximately halfway full with the 0.6 mM solution. Insert the vial into the stand. Replace the Cyclic Voltammetry System with the SPE attached in the stand.
15. Set the voltammetry parameters to the values in Table 6.

Table 6	
Number of segments	2
Initial potential (mV)	200
Switching potential 1 (mV)	–700
Final potential (mV)	200
Sweep rate (mV/s)	25
Current range	Low ($\pm 10 \mu\text{A}$)

16. Start data collection. When data collection is complete, name your sample appropriately.
17. With the knowledge you have from the previous steps, adjust any of the values to obtain the optimal voltammogram. Record your final optimized parameters.
18. Obtain voltammograms of RuHex at various concentrations.
 - a. Once you have optimized your data collection settings for the 0.6 mM sample of RuHex, repeat the data collection process and optimization for the remaining samples, including the sample of unknown concentration. Name each data set appropriately.
 - b. Analyze the voltammograms to obtain the anodic peak current (μA) for each sample. Record the anodic peak current (μA) in Table 9.
19. When you are finished collecting all of your data, save or export your data as instructed. Carefully remove the Cyclic Voltammetry System from the stand by pulling back on the top tab. Dispose of the SPE as instructed. **Important:** Do not invert the Cyclic Voltammetry System with a damp SPE attached. You want to avoid getting liquid inside the SPE connector.

DATA TABLE

Table 7		
Parameter modification	Observation	Sketch of voltage vs. time graph
Starting parameters		
Segment and voltage change		
Sweep rate change		
Current change		
Final optimized parameters		

Table 8		
Sweep rate (mV/s)	i_{pa} , anodic peak current (μ A)	i_{pc} , cathodic peak current (μ A)
25		
50		
100		
200		
300		
400		
500		

Table 9	
Concentration (mM)	i_{pa} , anodic peak current (μ A)
0.6	
1.2	
3.0	
6.0	
unknown	

DATA ANALYSIS

1. What set of parameters resulted in the best voltammogram?
2. Plot i_{pc} vs. $v^{1/2}$. Plot i_{pa} vs. $v^{1/2}$. This can be done using Manual Entry mode in Graphical Analysis app. Use the curve fit functions in Graphical Analysis to fit the data.
3. From the Nernst Equation, a fully reversible electrochemical redox molecule will exhibit a separation between reduction and oxidation peaks that is equal to 59 mV per electron transferred. Review the data you collected and measure the ΔE_p for the optimized CV of 0.6 mM RuHex obtained at 25 mV/s. Discuss whether or not this reaction exhibits electrochemical reversibility.
4. Determine the concentration of your unknown sample by plotting peak current versus RuHex concentration. This can be done using Manual Entry mode in Graphical Analysis app. Use the linear fit function to fit the calibration curve to the data. Use this information to determine the concentration in your unknown solution. The interpolate feature in Graphical Analysis can also be used.