

Using RuHex in Quantitative Cyclic Voltammetry

This experiment is a great introduction to understanding cyclic voltammetry. Students will observe how changes in the instrument's settings alter the voltammogram. They will also explore fundamental aspects of a voltammogram and learn how voltammograms can be used to understand a redox system.

ESTIMATED TIME

We estimate that this experiment can be completed in one, 3-hour class period.

TIPS

1. In the Electronic Resources you will find PDF and word-processing files of the student experiment. You can print the PDF, distribute it to students electronically, or post the file to a password-protected class web page or learning management system. Edit the word-processing file if you would like to tailor the experiment to suit your equipment and students. Sign in to your account at www.vernier.com/account to access the Electronic Resources.
2. It is prudent to try this experiment with the solutions you have prepared prior to giving the solutions to your students to ensure proper concentrations and experimental parameter setting.
3. If students get a signal greater than 2 μA for their 0.1 mM potassium chloride solution, replace the SPE with a new one.
4. Here are some generic troubleshooting tips if the voltammogram has additional peaks or if signal saturation occurs:
 - a. While testing your solution before giving it to the students, make sure the recommended parameters in the student instructions are still appropriate. You may want to modify the Switching Potentials.
 - b. A fouled electrode cannot accurately measure the RuHex solution because the effective electrode area decreases. If you or your students start to see irregular peaks, it is best to switch out the SPE.
 - c. If the voltammogram stops plotting in the middle of a run, it is likely that your sample is too concentrated, dilute your sample and rerun.
 - d. If the voltammogram is too noisy, consider changing the current setting in the parameters.

HAZARD ALERTS

The chemical safety signal words used in this experiment (**DANGER** and **WARNING**) are part of the Globally Harmonized System of Classification and Labeling of Chemicals (GHS). Refer to the Safety Data Sheet (SDS) that came with the chemical for proper handling, storage, and disposal information. SDS can also be found online from the manufacturer.

Hexaammineruthenium(III) chloride, 6.0 mM, $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$: **WARNING**: Causes skin irritation, causes serious eye irritation, may cause respiratory irritation.

Potassium chloride, 1.0 M, KCl: This chemical is considered nonhazardous according to GHS classifications. Treat all laboratory chemicals with caution. Prudent laboratory practices should be observed.

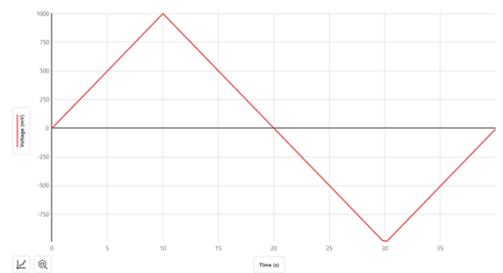
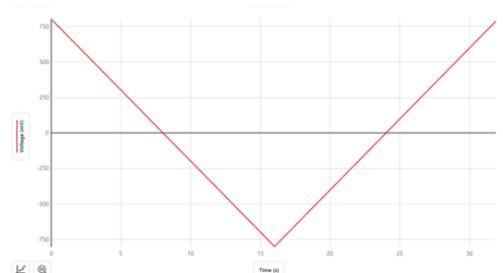
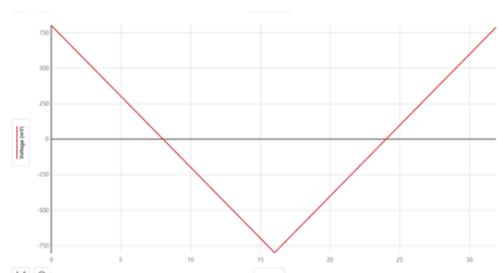
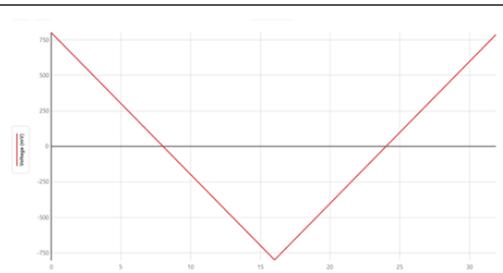
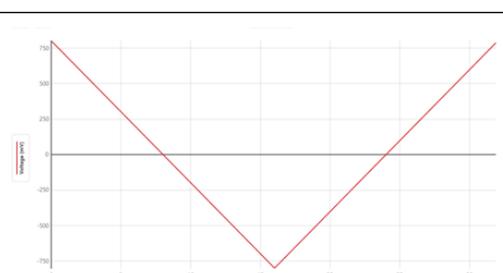
ANSWER TO PRE-LAB ACTIVITY

Students should use $M_1V_1 = M_2V_2$ and present their plan for how to prepare the required solutions via serial dilution.

M_1 (mM)	V_1 (mL)	M_2 (mM)	V_2 (mL)
6.0	10.0	3.0	20.0
6.0	4.0	1.2	20.0
6.0	2.0	0.6	20.0

1. To prepare 20 mL of a 3.0 mM solution from the 6.0 mM RuHex stock solution, mix 10.0 mL of 6.0 mM stock solution with 10.0 mL of 0.1 potassium chloride solution.
2. To prepare 20 mL of a 1.2 mM solution from the 6.0 mM RuHex stock solution, mix 4.0 mL of 6.0 mM stock solution with 16.0 mL of 0.1 potassium chloride solution.
3. To prepare 20 mL of a 0.6 mM solution from the 6.0 mM RuHex stock solution, mix 2.0 mL of 6.0 mM stock solution with 18.0 mL of 0.1 potassium chloride solution.

DATA TABLE

Parameter modification	Observation	Sketch of voltage vs. time graph
Starting parameters	Very noisy trace; it extends too far in the anodic direction and the cathodic direction. The anodic peak is around -150 mV and the cathodic peak is around -250 mV.	
Segment and voltage change	The anodic and cathodic ends were appropriately captured. This change made the voltammogram appear much more duck-like.	
Sweep rate change	The signal took much longer to acquire. It was also smaller in amplitude with a sweep rate of 25 mV/s compared to the previous 100 mV/s.	
Current change	The signal was cleaner. However, if the signal got too large for the current range, the data could not be collected. It was a fine balance between sweep rate, current, and concentration of the sample.	
Final optimized parameters	Table 6 gave good results. In some cases, I shortened Switching potential 1 to -600 mV.	

Sweep rate (mV/s)	i_{pa} , anodic peak current (μA)	i_{pc} , cathodic peak current (μA)
25	105.02	-157.04
50	153.42	-208.27
100	218.58	-288.31
200	303.57	-403.99
300	368.50	-486.62
400	423.51	-550.37
500	465.53	-607.74

Concentration (mM)	i_{pa} , anodic peak current (μA)
0.6	11.33
1.2	21.97
3.0	49.64
6.0	97.21
unknown	34.17

SAMPLE VOLTAMMOGRAMS

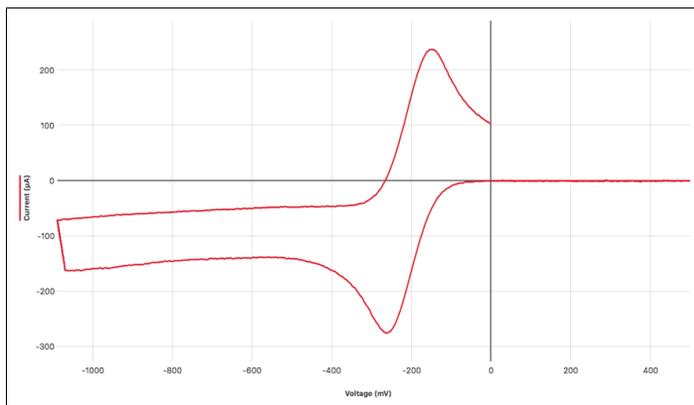


Figure 1 CV of 6.0 mM RuHex solution, non-optimized parameters

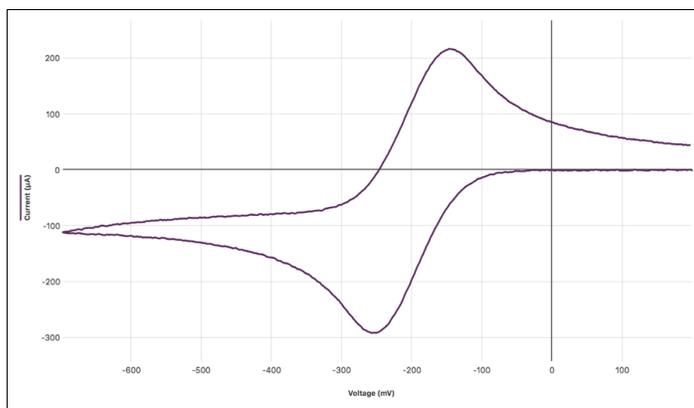


Figure 2 CV of 6.0 mM RuHex solution, segment and potential optimized

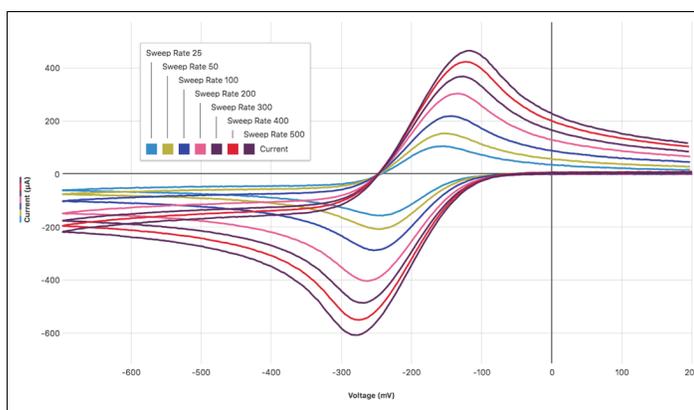


Figure 3 CV of 6.0 mM RuHex solution at various scan rates

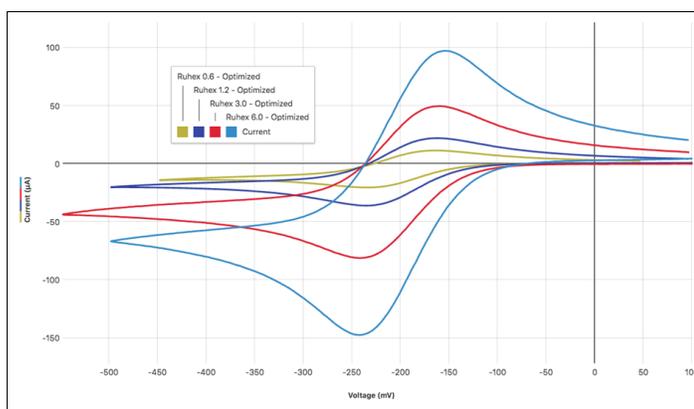


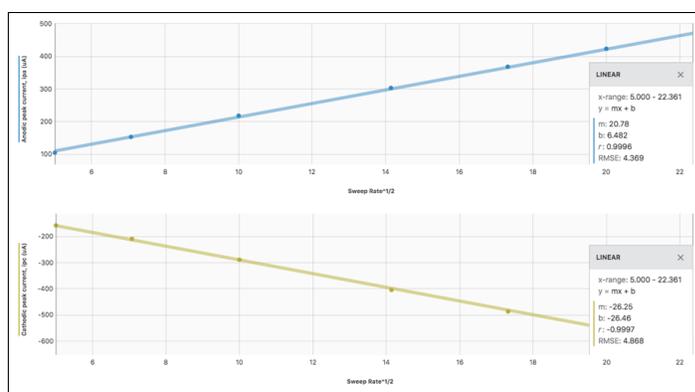
Figure 4 CV of RuHex solution at various concentrations

ANSWERS TO ANALYSIS QUESTIONS

1.

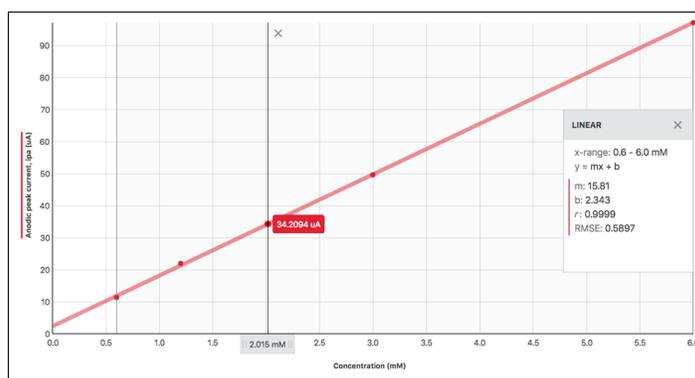
Optimized Parameters	
Number of segments	2
Initial potential (mV)	100
Switching potential 1 (mV)	-500
Final potential (mV)	100
Sweep rate (mV/s)	50
Current range	Medium ($\pm 100 \mu\text{A}$)

2.



3. At a scan rate of 25 mV/s, the ΔE_p for the 0.6 mM RuHex sample is 72 mV. Ideally, this value would be 57 mV at 25°C per electron transferred. Therefore, the reaction is fairly reversible with the ΔE_p . The most likely reason for this deviation is due to the surface of the SPE. Cleaning the electrode may help improve this value.

4.



In the sample data presented here, the peak current for the unknown sample measured 34.17 μA . The calibration curve resulted in the following equation:

$$\text{peak current} = 15.81 \times \text{concentration} + 2.343$$

Therefore, the concentration of the unknown sample is 2.0 mM.