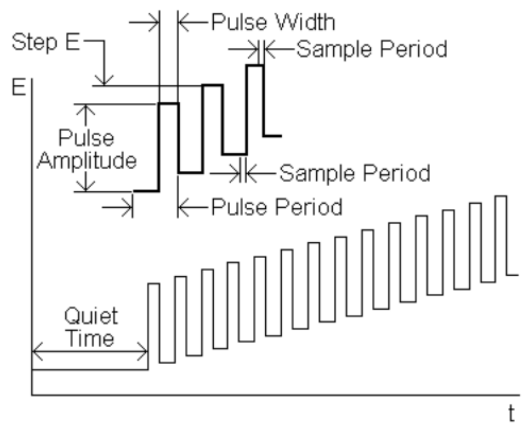
Analysis of Ferrocene by Differential Pulse Polarography (DPP) and Square Wave Polarography (SWP)

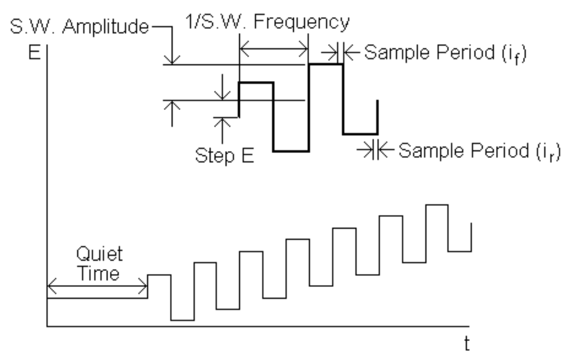
Background:

DPP (DPV) and SWP (SWV) are two closely related techniques. These techniques take advantage of fast computer timing to sample current signals at two narrow regions (relative to the time of application) of a voltage pulse at the working electrode. The current is sampled at two points within a pulse. The difference of a pair of current values is mainly composed of the Faradaic component of the electrode process occurring at the working electrode.

In the DPP the plot of difference of the sampled currents vs. applied voltage resembles a derivative curve. SWV plot resembles a derivative curve as well.



DPP excitation potential wave.



SWP excitation potential wave.

Apparatus:	Potentiostat, glassy carbon mini electrode, Ag/AgCl(s) KCl (satd) electrode, platinum auxiliary electrode, nitrogen cylinder, oxygen absorber, polishing material, Eppendorf pipettes, 15ml and 5mL pipettes, 50mL and 100mLvolumetric flasks.
Chemicals:	0.100M Ferrocene in 0.1M sodium perchlorate/acetonitrile (stock), 0.1M sodium perchlorate/acetonitrile

Electrochemical Cell:

- Working electrode: Glassy carbon mini electrode (1mm diameter)
- Auxiliary electrode :Pt
- Analyte matrix :0.1M sodium perchlorate /acetonitrile
- Reference (Ag) electrode filling :0.1M sodium perchlorate /acetonitrile

Procedure:

This experiment will be done on a glassy carbon mini electrode. Polish the electrode surface to a mirror finish with alumina slurry and clean the surface well (sonicate) with DI water. Prepare 100.00 ml of a ferrocene solution of concentration 5.0 mM in 0.1M solution of sodium perchlorate in acetonitrile (solvent) using the stock solution of ferrocene (0.100M). Prepare a 10mM working standard (50.00mL) solution of ferrocene in 0.1M solution of sodium perchlorate in acetonitrile.

Starting set of parameters are given in a table below. If the parameters are unsuitable change them appropriately. Each run must be saved in separate (named) file.

Set up the three electrode system (experimental parameters given below) and fill the cell with the 5mM ferrocene (15mL) in 0.1M sodium perchlorate/acetonitrile. Expel dissolved oxygen in the solution by passing 'oxygen free nitrogen' through this 'test' solution. Stop the purging of oxygen through the solution but maintain an envelope of nitrogen over the solution. Let the solution achieve quiescence. Set the parameters for DPP (and later for SWP) from the software provided with the potentiostat. Connect the electrodes to the potentiostat appropriately, perform DPP and later SWP.

I. In the DPV mode, investigate the effect of pulse amplitude on the peak current ip by varying the pulse amplitude 5mV, 10mV, ... using the 5.00mM ferrocene solution (15.00ml). Save all runs in separate named files. Remember to stir the solution (0.5 min) before each run and allow it to attain quiescence for 10 seconds.

II. In the SWV mode, investigate the effect of SW amplitude, by varying this parameter in a systematic manner, for example 5, 10, 25, 30, 50, 75, 100, 125mV, on the 5mM ferrocene (15.00ml) solution. Remember to stir the solution (0.5min) before each run and allow it to attain quiescence for 10 seconds.

III. Prepare a test solution by diluting 1:100 of a sample of the unknown solution (test solution). Using 15 mL of the test solution run the DPP followed by SWP analysis under the parameters given below (you may change parameters to optimize the signal based upon I and II above). Save the data in a named file. Add 10ul aliquot of 100mM standard to the solution (standard addition). Repeat four more standard additions of 10ul aliquots. Save all data files. Remember to stir the solution (0.5min) before each run and allow it to attain quiescence for 10 seconds.

Differential Pulse and Square Wave Voltammetry Experimental Parameters etc.:

SWP experiment		DPP experiment	
Initial E, mV	100	Initial E, mV	100
Final E, mV	800	Final E, mV	800
Quiet time, s	2	Quiet time, s	2
Full scale	10 mA	Full scale, uA	10mA
Step E, mV	4	Step E, mV	4
SW Amplitude, mV	25	Pulse width, ms	50
SW Frequency, Hz	15	Pulse Period, ms	200
Sample Period	1 mSecond	Pulse Amplitude,	10mV
Filter	100 Hz	Sample Period	1 mSecond
		Pulse Type	-

Every time a parameter is changed, to save the new parameter [Apply] before [Exit].

Treatment of data:

1. Open each of the data files and 'smoothen' each plot and save the files.
2. Determine the peak heights for each run in part I and generate a suitable plot to show the effect of pulse height on i_p.
3. Determine the peak heights for each run in part II and generate a suitable plot to show the effect of pulse height on i_p.
4. Determine the peak heights for the two modes of analysis run in part III. Generate respective standard addition plots.
5. Use the plots from the previous step to determine the concentration of the unknown solution of ferrocene from DPP and SWP techniques.

Standard Addition Calculations: Electrochemistry Experiments

Volume of unknown solution used = V_u
Cumulative volume of standard added = V_s
Concentration of unknown = C_u
Concentration of standard = C_s
Current peak (response from a solution) = i

Plot i vs V_s

Derivation of Standard Addition Plot Equation

$$For\ Signal = i$$

$$i = kC$$

$$i = k\frac{(C_u V_u + C_s V_s)}{(V_u + V_s)}$$

$$i = \frac{kC_u V_u}{V_u + V_s} + \frac{kC_s V_s}{V_u + V_s}$$

$$i = kC_u + \frac{kC_s}{V_u} V_s$$ for the case $V_s << V_u$ from; $i = \frac{kC_u V_u}{V_u + V_s} + \frac{kC_s V_s}{V_u + V_s}$

$$0 = kC_u + \frac{kC_s V_{s@i=0}}{V_u}$$ would yield the x intercept, $V_{s@i=0}$

$$C_u = -\frac{C_s V_{s@i=0}}{V_u}$$ upon rearrangement