Lecture IV
Calibration

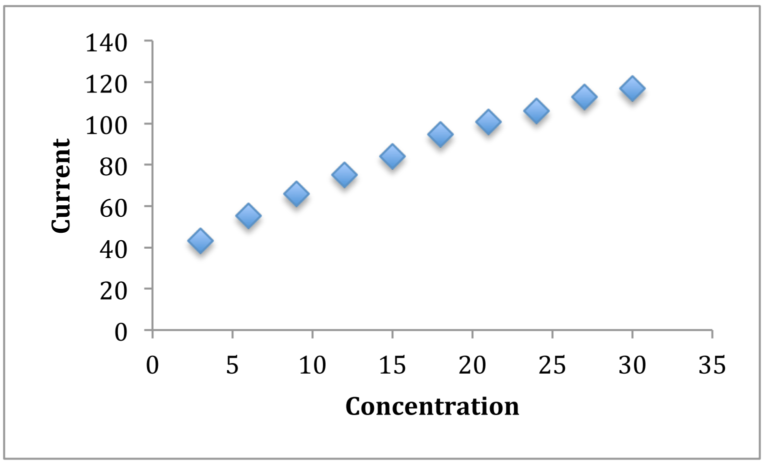
PROBLEM 1 Data from chronoamperometry obtained with a Pt bare electrode (WE diameter 1mm), functionalized with MWCNTs and glucose oxidase, in presence of increasing concentrations of glucose are in the table:

StDev (nA)	Concentration (mM)	Current (nA)
0.15	3	43.35
0.23	6	55.23
0.13	9	65.82
0.17	12	75.13
0.17	15	83.95
0.07	18	94.66
0.53	21	100.91
0.39	24	105.97
0.44	27	112.79
0.28	30	116.97

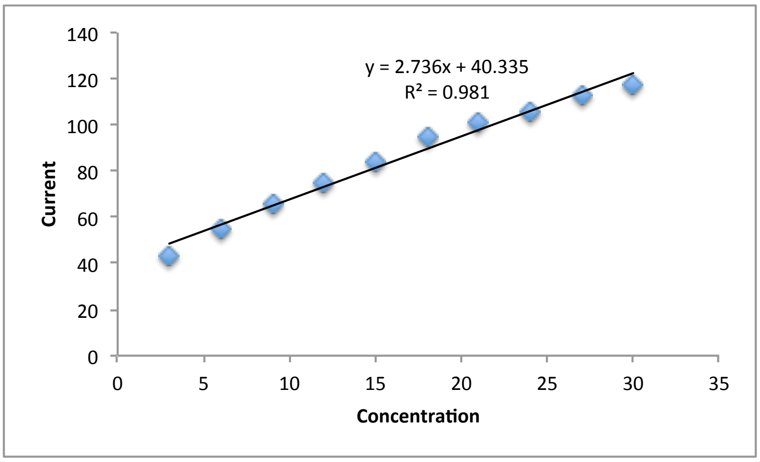
1. Plot the data.
2. Compute the regression analysis (slope, intercept, R2).
3. Plot the residual plot. Is the linear regression appropriate?
3. Which is the linearity range?
4. Calculate the Sensitivity, defined in the correct linear range.

SOLUTION

1.



2. Regression Line



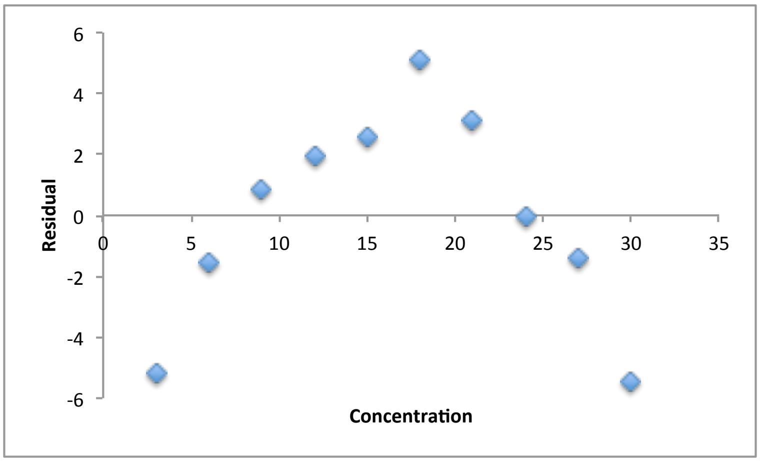
Slope = 2.736

Intercept = 40.335

R^2 = 0.981

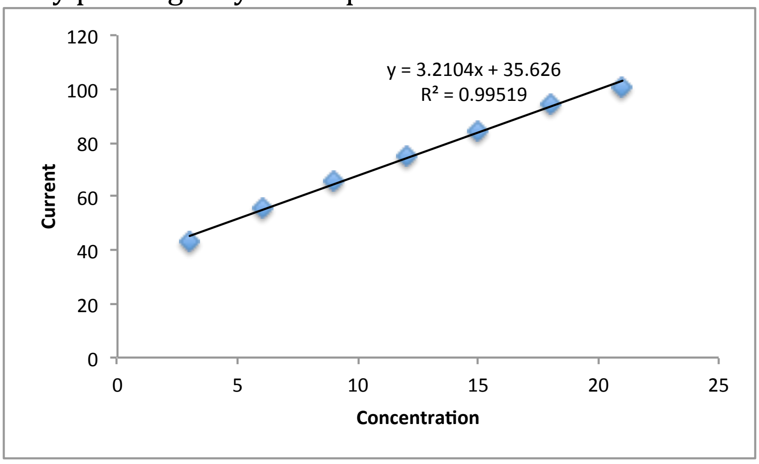
3. In regression analysis, the difference between the observed value of the dependent variable (y) (Current) and the predicted value (ŷ) (Linear Regression Value) is called the residual (e). Each data point has one residual: Residual = Observed value - Predicted value

Concentration	Observed Current	Regression Line (Predicted) Y=2.736*X+40.335	Residual= Observed-Predicted
3	43.35	48.543	-5.193
6	55.23	56.751	-1.521
9	65.82	64.959	0.861
12	75.13	73.167	1.963
15	83.95	81.375	2.575
18	94.66	89.583	5.077
21	100.91	97.791	3.119
24	105.97	105.999	-0.029
27	112.79	114.207	-1.417
30	116.97	122.415	-5.445



The residual plot is a graph that shows the residuals on the vertical axis and the independent variable on the horizontal axis. If the points in a residual plot are randomly dispersed around the horizontal axis, a linear regression model is appropriate for the data; otherwise, a non-linear model is more appropriate.
The obtained plot pattern is non-random (inverted U-shaped), suggesting a better fit for a non-linear model.
(http://stattrek.com/statistics/dictionary.aspx?definition=Residual%20plot)

5. By plotting only first 7 point we have:



Slope = 3.21
Intercept = 35.626
R^2 = 0.995

In this case if we redo the residual plot, we will have a random pattern!

So we can define the linear range between 3 and 21mM, with a sensitivity of 3.21nA/mM

Sensitivity

PROBLEM 2

Compute the sensitivity for hydrogen peroxide detection in chronoamperometry. Consider electrode diameter of 4mm.

Start from the Cottrell equation

$$i = \frac{nFAC\sqrt{D}}{\sqrt{\pi t}}$$

i = current, in unit A
n = number of electrons (to reduce/oxidize one molecule of analyte)
F = Faraday constant, 96'485 C/mol
A = area of the (planar) electrode in cm^2
C = concentration of the reducible analyte in mol/cm^3;
D = diffusion coefficient for species in cm^2/s
t = time in s.

For hydrogen peroxide we have

$$H_2O_2 + 2H^+ + 2e^- \Leftrightarrow 2H_2O$$

So *n=2*. Δt is the time interval between metabolite injection and current-increment measure, that we can approximate as $t = 5s$. For hydrogen peroxide, $D = 1.43 \cdot \frac{10^{-5} cm^2}{s}$.

SOLUTION

The area $A = 0.1256 cm^2$.

So the theoretical sensitivity is

$$S = \frac{nFA\sqrt{D}}{\sqrt{\pi \Delta t_0}} = \frac{2 \cdot 96485 C/mol \cdot 0.1256 cm^2 \cdot \sqrt{1.43 \cdot \frac{10^{-5} cm^2}{s}}}{\sqrt{\pi \cdot 5}}$$

$$= 23.12\ A \cdot \cancel{cm^3}/mol$$

PROBLEM 3

Compute the theoretical sensitivity for hydrogen peroxide detection in cyclic voltammetry. Consider electrode diameter of 4mm and a scan rate of 100mV/s.

Consider the Randles-Sevčik equation:

$$i_p = 0.4463nFAC\sqrt{\frac{nFDv}{RT}}$$

Where v is the scan rate (V/s), T the temperature in Kelvin, R the gas constant (8.314 VC/Kmol), i_p the peak current. If the solution is at room temperature:

$$i_p = 2.686 \cdot 10^5 \cdot C \cdot n^{3/2} A D^{1/2} v^{1/2}$$

SOLUTION

$$S = \frac{\Delta i}{\Delta c} = 2.686 \cdot 10^5 \cdot 2^{3/2}(0.1256cm^2)\left(1.43 \cdot \frac{10^{-5}cm^2}{s}\right)^{1/2}\left(\frac{0.1V}{s}\right)^{1/2}$$

$$= 114.11\ A \cdot \cancel{cm^3}/mol$$