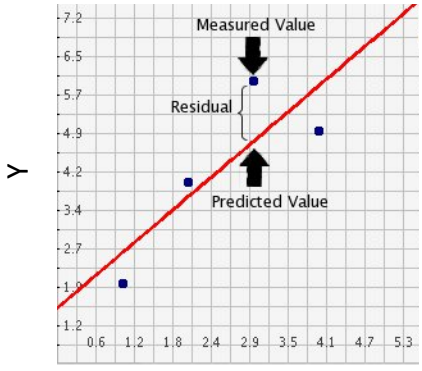
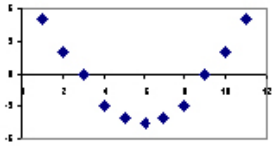
Curve fitting and statistics

In regression analysis, the difference between the observed value of the dependent variable *y* and the predicted value $\hat{y}$ (Linear Regression Value) is called the **residual *e***. Each data point has one residual.

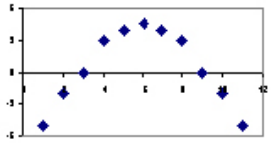


The **residual plot** is a graph that shows the residuals on the vertical axis and the independent variable on the horizontal axis. If the points in a residual plot are randomly dispersed around the horizontal axis, a linear regression model is appropriate for the data; otherwise, a non-linear model is more appropriate.

In the plots below, the residuals are not randomly dispersed, so a non-linear model must be used.

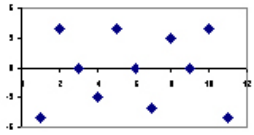


Non-random: U-shaped curve



Non-random: Inverted U

In the plot below the residuals are randomly dispersed, so the linear fitting is good.



Random pattern

The **coefficient of determination R^2** is used to express how well the observed outcomes are predicted by the model.

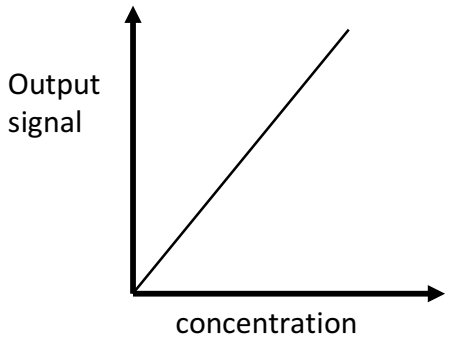
Coefficient of determination. The coefficient of determination (R^2) for a linear regression model with one independent variable is:

$$R^2 = \{ (1 / N) * \Sigma [(x_i - \bar{x}) * (y_i - \bar{y})] / (\sigma_x * \sigma_y) \}^2$$

where N is the number of observations used to fit the model, Σ is the summation symbol, x_i is the x value for observation i, $\bar{x}$ is the mean x value, y_i is the y value for observation i, $\bar{y}$ is the mean y value, σ_x is the standard deviation of x, and σ_y is the standard deviation of y.

Calibration curve and sensitivity

In analytical chemistry, a **calibration curve** is a general method for determining the concentration of a substance in an unknown sample by comparing the unknown to a set of standard samples of known concentration. In practice, you make a plot signal vs concentration. It is then possible to measure the response of the unknown and, using the calibration curve, interpolate to find its concentration.

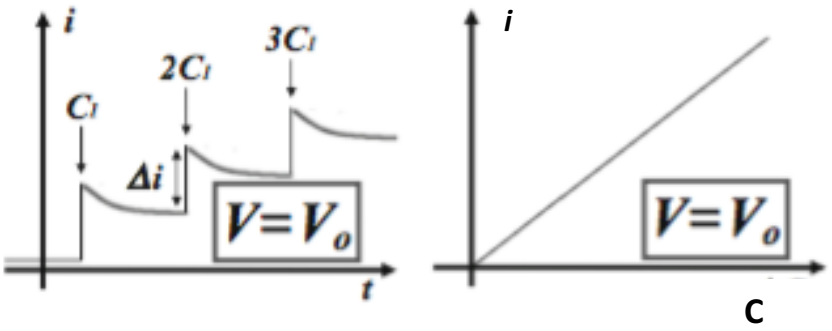


The output signal is different depending on the different types of sensors used. Electrochemical sensors transform the effect of the electrochemical interaction analyte-electrode into a useful signal (for instance current, voltage, impedance).

The slope gives the sensitivity of the sensor.
Sensitivity = output signal /measured property (in our case the concentration C)

Chronoamperometry

In chronoamperometry, you measure the current response in a controlled potential experiments. Typically, you apply a constant voltage to the working electrode, and you measure the current variations when adding solute to the sample solutions (left figure).



C

The height of the current steps shows a linear dependency on the solute concentration, as described by **Cotrell equation**:

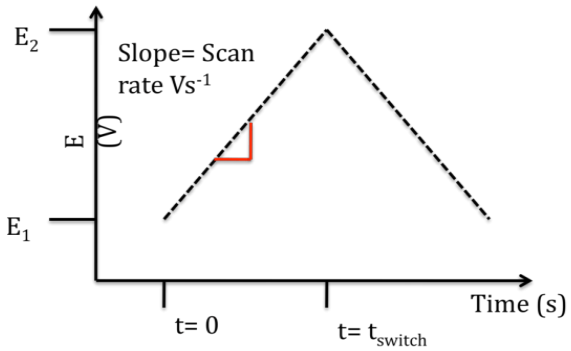
$$i = \frac{nFAC\sqrt{D}}{\sqrt{\pi t}}$$

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.

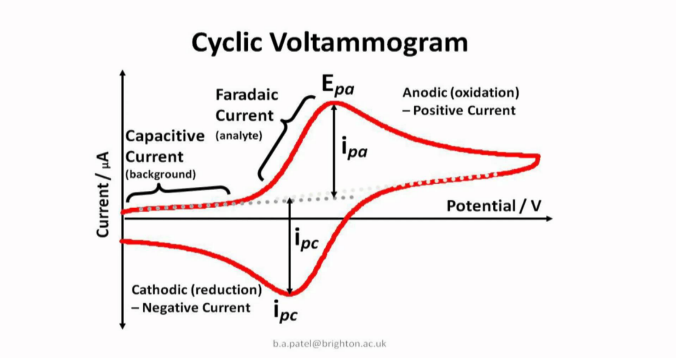
Consequently, you can build a calibration curve by plotting the current versus the concentration (right figure).

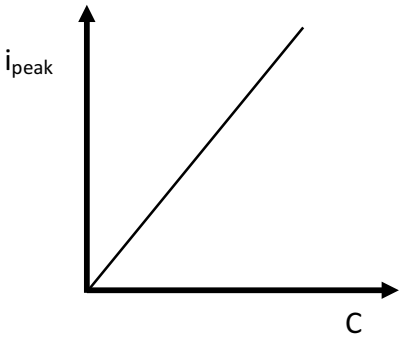
Cyclic voltammetry

In a cyclic voltammetry experiment, the working electrode potential is ramped linearly versus time in the forward and backward direction to come back to the initial potential (see waveform below).



The current at the working electrode is plotted versus the applied voltage to give a cyclic voltammogram (left figure).





These cycles of ramps can be repeated multiple times successively.
The peak current steps shows a linear dependency on the solute concentration, as described by **Randles-Sevcik equation**

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

where ip is the peak current (A)
n is the number of electrons transferred per mole (mol e-)
F is the Faraday constant (96489 C/mol e-)
A is the electrode area (cm2)
C is the concentration (mol/cm3)
D id the diffusion coefficient (cm2/s)
v is the scan rate (V/s)
T temperature in K
R gas constant

Consequently, you can build a calibration curve by plotting the peak current versus the concentration (right figure).

At room temperature you can simplify the Randels-Sevcik equation as:

$$I_P = 2,686 \cdot 10^5 \cdot z^{3/2} A D^{1/2} C v^{1/2}$$