Chem 115

Instrumental Analysis and Bioanalytical Chemistry

Lecture 3: Analysis and Solution Chemistry

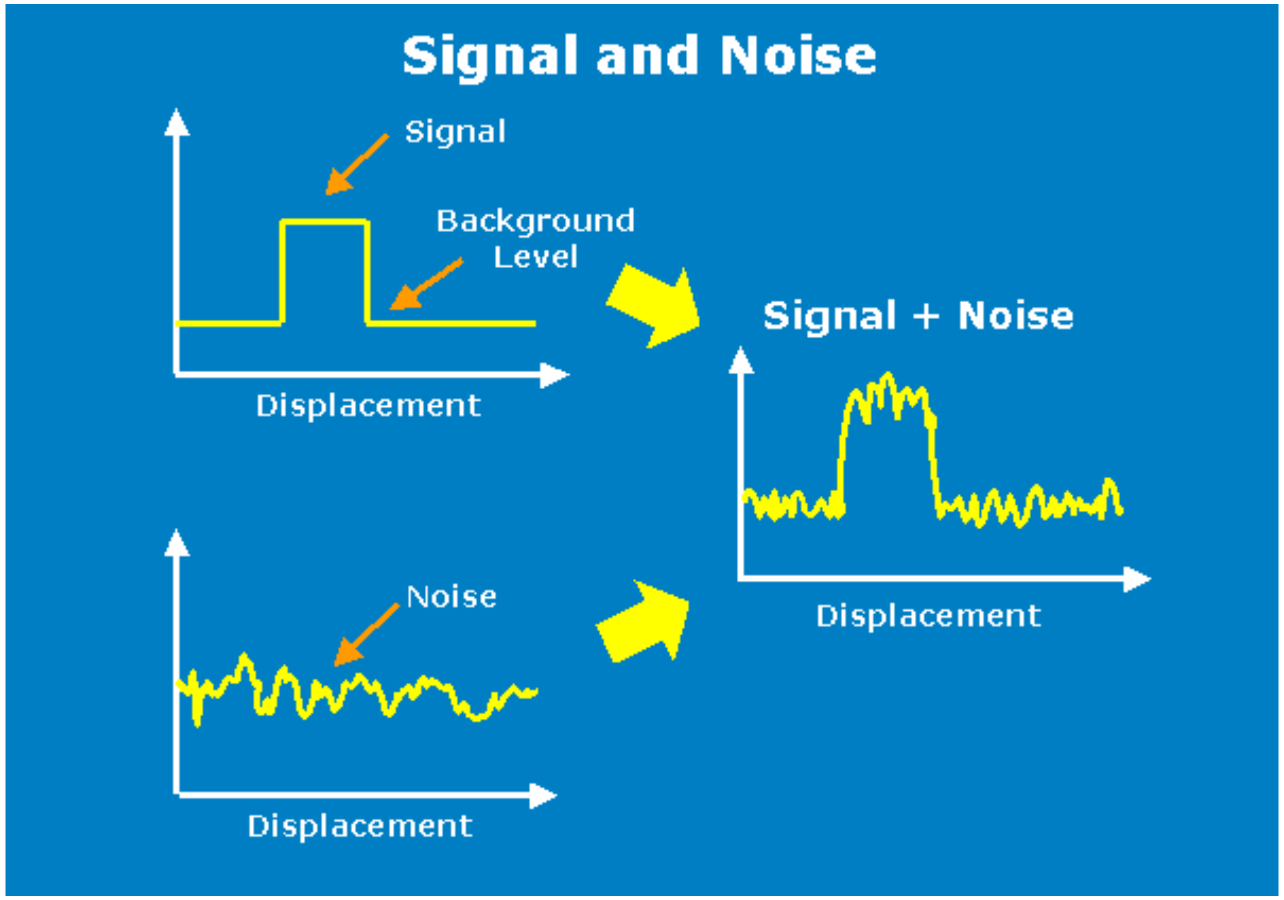
What’s in this lecture?

- Noise
- Calibration curves
- Solution chemistry

Example Time...

	% Analyte			
	Analyst 1	Analyst 2	Analyst 3	Analyst 4
Sample 1	10.0	8.1	13.0	13.0
Sample 2	10.2	8.0	10.2	8.0
Sample 3	10.0	8.3	10.3	7.9
Sample 4	10.2	8.2	11.1	12.4
Sample 5	10.1	8.0	13.1	10.3
Sample 6	10.1	8.0	9.3	9.0
Mean	10.1	8.1	11.2	10.1
Std. Dev.	0.089	0.13	1.57	2.2

Signals vs. noise



$$\frac{S}{N} = \frac{\bar{x}}{s} = \frac{1}{RSD}$$

- Noise determines minimum signal that can be detected, i.e. limit of detection (LOD).
- Also determines limit of quantitation (LOQ)

Noise types

- White noise (frequency independent)
  - Thermal noise
  - Shot noise
- Flicker noise (frequency dependent)
  - Drift
  - Pink noise
  - Red noise
- Environmental noise

Noise solutions

- Hardware devices for isolation and filtering.
- Signal averaging.
- Fourier transform.

$$\frac{S}{N} = \frac{\bar{x}}{s} = \frac{1}{RSD}$$

Calibration curves...

- Regression analysis is used to find the curve that fits the data points the best
- The simplest regression analysis is linear least-squares analysis, which gives the equation for the best straight line for a set of (x,y) points.
- This assumes a line is the best fit, and only works for 2-D plots.
- Higher order regression analysis can be done by software.

Least squares fit...

$$S_{xx} = \sum (x_i - \bar{x})^2 = \sum x_i^2 - \frac{(\sum x_i)^2}{N}$$
$$S_{yy} = \sum (y_i - \bar{y})^2 = \sum y_i^2 - \frac{(\sum y_i)^2}{N}$$
$$S_{xy} = \sum (x_i - \bar{x})(y_i - \bar{y}) = \sum x_i y_i - \frac{(\sum x_i)(\sum y_i)}{N}$$

For a line with equation y = mx + b

$$m = \frac{S_{xx}}{S_{yy}}$$

$$s_b = s_r \sqrt{\frac{\sum x_i^2}{N \sum x_i^2 - (\sum x_i)^2}} = s_r \sqrt{\frac{1}{N - \frac{(\sum x_i)^2}{\sum x_i^2}}}$$

$$b = \bar{y} - m\bar{x}$$

$$s_r = \sqrt{\frac{S_{xx} - m^2 S_{yy}}{N-2}}$$

$$s_m = \sqrt{\frac{s_r^2}{S_{xx}}}$$

$$s_c = \frac{s_r}{m} \sqrt{\frac{1}{M} + \frac{1}{N} + \frac{(\bar{y}_c - \bar{y})^2}{m^2 S_{xx}}}$$

Solution Chemistry...

Brønsted-Lowry acids and bases

- Brønsted-Lowry acids are proton donors.
- Brønsted-Lowry bases are proton acceptors.
- To behave as an acid, a base must be present, and vice versa.
- When an acid donates a proton, it forms a conjugate base.
- When a base accepts a proton, it forms a conjugate acid.
- Some substances are amphiprotic, they can behave as an acid or a base.

Strengths of acids and bases

Strongest acid ↑ / Weakest base

Weakest acid ↓ / Strongest base

acid 1		base 2		acid 2		base 1
$HClO_4$	+	H_2O	$\rightarrow$	H_3O^+	+	ClO_4^-
HCl	+	H_2O	$\rightarrow$	H_3O^+	+	Cl^-
H_3PO_4	+	H_2O	$\leftrightarrow$	H_3O^+	+	$H_2PO_4^-$
$HC_2H_3O_2$	+	H_2O	$\leftrightarrow$	H_3O^+	+	$C_2H_3O_2^-$
$H_2PO_4^-$	+	H_2O	$\leftrightarrow$	H_3O^+	+	HPO_4^{2-}
NH_4^+	+	H_2O	$\leftrightarrow$	H_3O^+	+	NH_3

The equilibrium state

$$H_3AsO_4 + 3I^- + 2H^+ \leftrightarrow H_3AsO_3 + I^{3-} + H_2O$$

After reaching equilibrium, what happens if we add more H_3AsO_4?

The equilibrium state

If:

$$wW + xX \leftrightarrow yY + zZ$$

Then:

$$K = \frac{[Y]^y [Z]^z}{[W]^w [X]^x}$$

Important equilibria in analytical chemistry

Type of equilibrium	Name and Symbol	Example	Expression
Water dissociation	Ion-product constant, K_w	$2\ H_2O \leftrightarrow H_3O^+ + OH^-$	$K_w = [H_3O^+][OH^-]$
Dissociation of slightly soluble species	Solubility product, K_{sp}	$BaSO_4(s) \leftrightarrow Ba^{2+} + SO_4^{2-}$	$K_{sp} = [Ba^{2+}][SO_4^{2-}]$
Weak acid or base dissociation	Dissociation constant, K_a or K_b	$CH_3COOH + H_2O \leftrightarrow CH_3COO^- + H_3O^+$	$K_a = \frac{[CH_3COOH]}{[CH_3COO^-][H_3O^+]}$
Formation of complex ion	Formation constant, K_F or β_n	$Ni^{2+} + 4\ CN^- \leftrightarrow Ni(CN)_4^{2-}$	$\beta_4 = \frac{[Ni(CN)_4^{2-}]}{[Ni^{2+}][CN^-]^4}$

p-Functions

$px = -\log(x)$

For instance:

$pH = -\log([H_3O^+])$
or
$pAg = -\log([Ag^+])$

Where's the water?

$$2\ H_2O \leftrightarrow H_3O^+ + OH^-$$

Why:

$$K_w = [H_3O^+][OH^-]$$

Not:

$$K_w = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$