Quality Assurance

These are the steps we take to get the right answer for our purpose.

The answer should have sufficient accuracy and precision to support subsequent decisions.

Raw data **= individual measurements**

Treated data **= concentrations derived from raw data using calibration curve.**

Results **= quantities reported after statistical analysis of treated data.**

Detection Figure of Merit – *Dynamic Range*

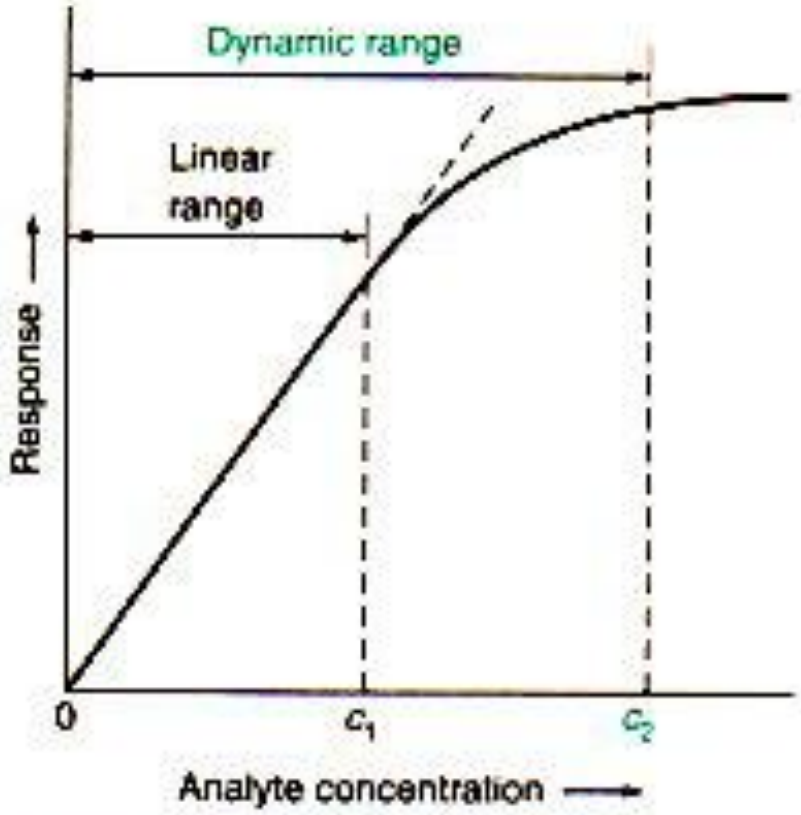
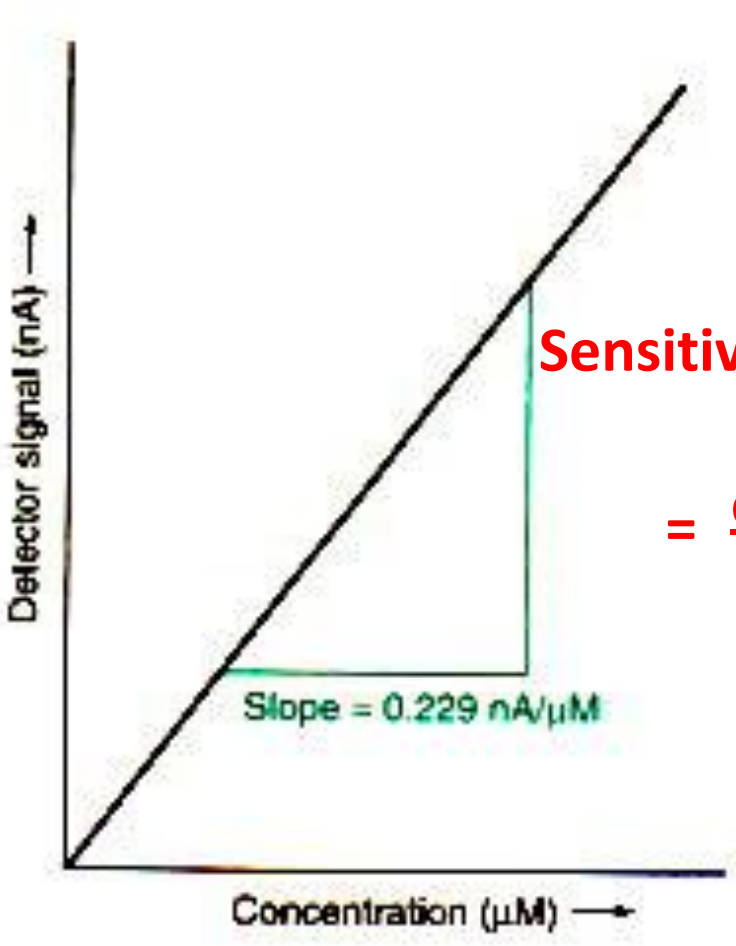


Figure 5-1 Schematic calibration curve with linear and nonlinear regions.

Detection Figure of Merit - *Sensitivity*



Sensitivity = slope of the calibration curve

$$= \frac{\text{change in detector signal}}{\text{change in analyte concentration}}$$

Calibration Curve for ClO_4^-

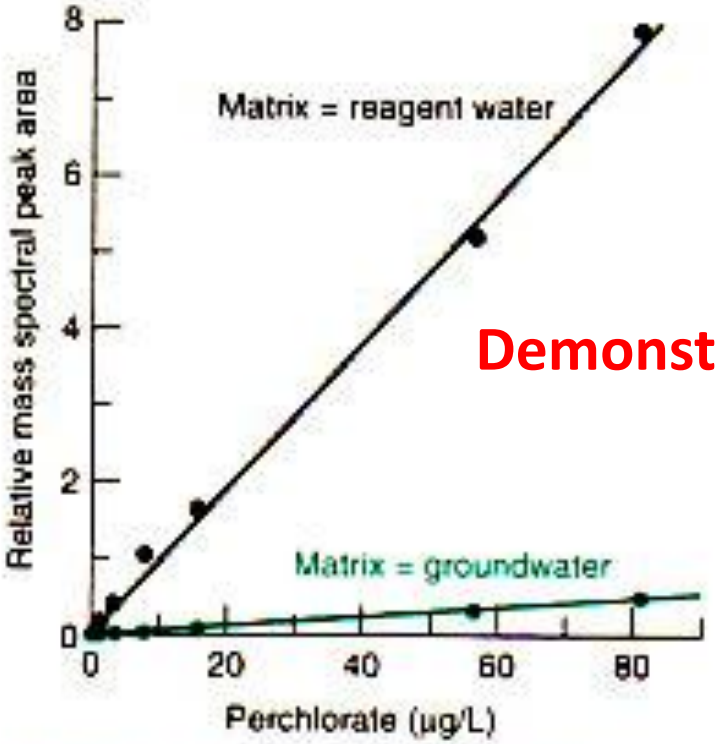


Figure 5-4 Calibration curves for perchlorate in pure water and in groundwater. [Data from C. J. Koester, H. R. Beller, and R. U. Halden, *Environ. Sci. Technol.* **2000**, *34*, 1862.]

Demonstrates a matrix effect

Detection Figures of Merit

Accuracy **= how close measured value is to expected (true) value.**
(gauge with calibration checks, reference standards, blanks)

Precision **= how reproducible the result is (*s*, *rsd*, <5%)**
(replicate samples, replicate portions of same sample)

Detection Limit **= minimum detectable concentration (= 3*s*/m)**

signal detection limit **-** $y_{dl} = y_{blank} + 3s$ **(3x greater than noise)**

Calibration line **-** $y_{sample} - y_{blank} =$ **m x sample conc.**

Quantitation limit **=** $(=10s/m)$ **(10x greater than noise)**

Ideal Detection Figures of Merit

- **Linear dynamic range** = 3-5 orders of magnitude
- **Response precision or variability** = RSD $\leq$ 5%
- **Accuracy** = not always possible to test. Must have true standard
- **Sensitivity** = all relative. Desire largest change in instrument signal per change in analyte concentration.
- **Limit of detection** = again all relative, but ppb-ppt is ideal for many analytes. (1 ppm = mg/L; 1 ppb = µg/L; 1 ppt = ng/L)

How Does One Related an Instrument Signal to an Analyte Concentration?

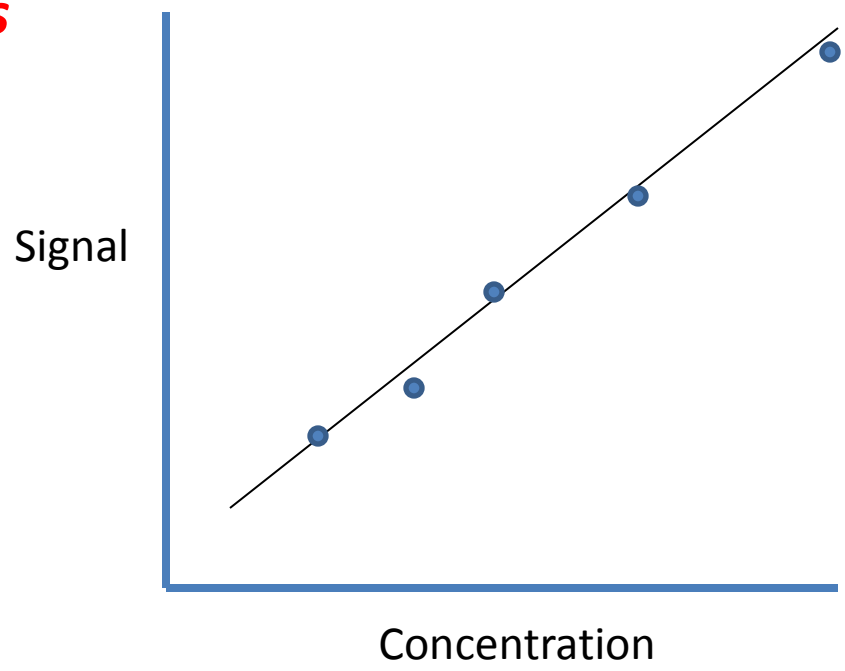
Calibration curve = Response curve

Standards and blanks

External standards

$$y = mx + b$$

signal Concentration



Practical when the matrix is not complex!!

Quantitation – *Standard Addition*

also referred to as *spiking*.

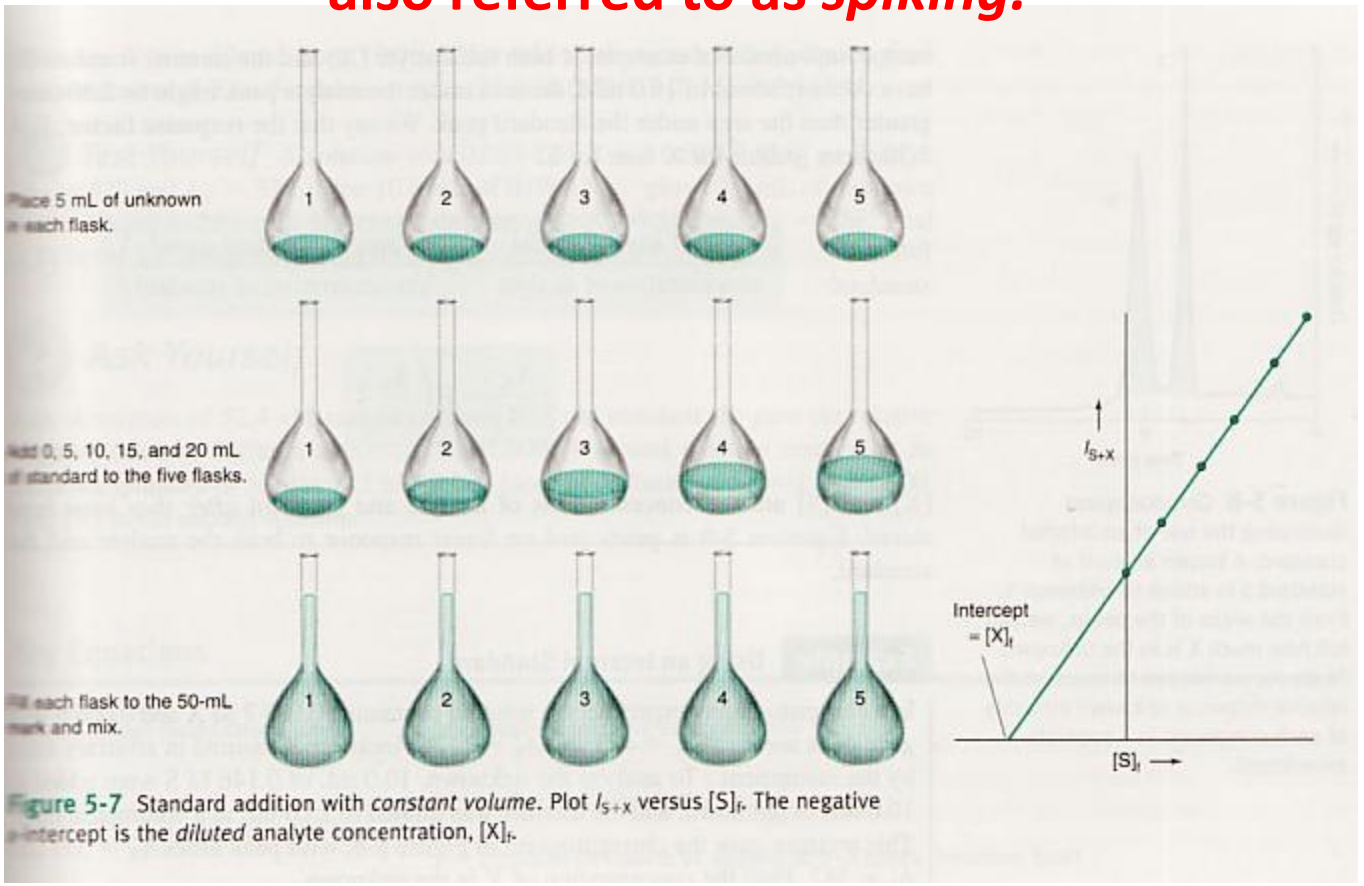
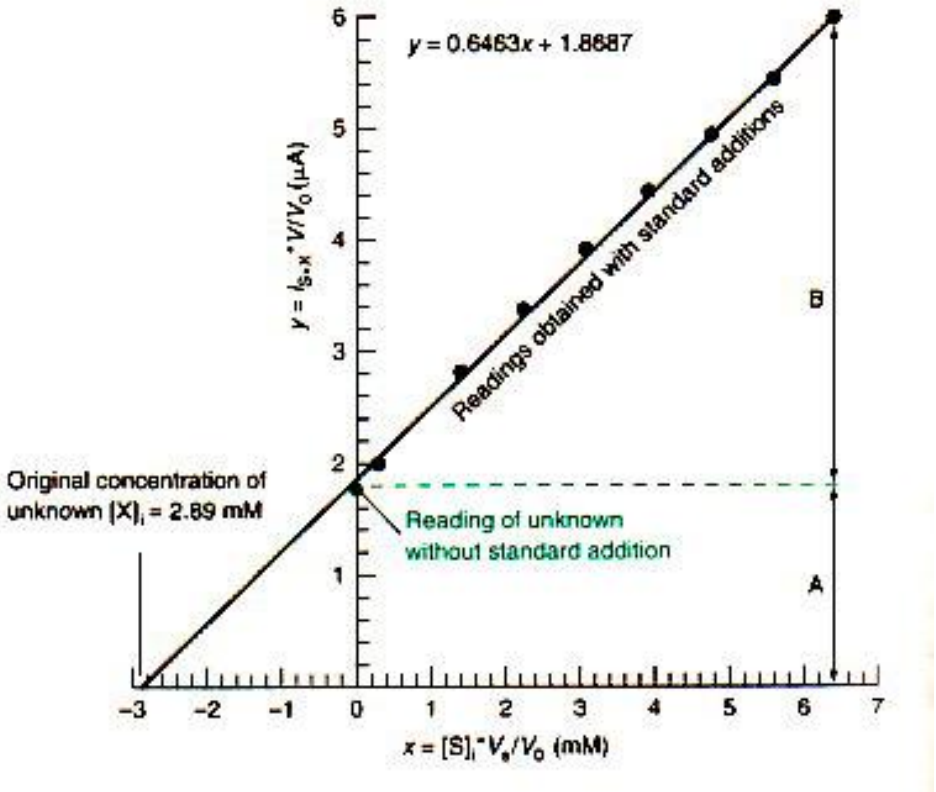


Figure 5-7 Standard addition with *constant volume*. Plot I_{S+X} versus $[S]_f$. The negative x-intercept is the *diluted* analyte concentration, $[X]_f$.

Practical when the matrix <u>is</u> complex!!

Quantitation – *Standard Addition*

Figure 5-6 Graphical treatment of standard addition using Equation 5-8 with increasing final volume. Standard additions should increase the original signal (A) by a factor of 1.5 to 3. That is, B = 0.5A to 2A.



Calibration – *Standard Addition*

$$\frac{\text{concentration of analyte in unknown}}{\text{concentration of analyte + standard in mixture}} = \frac{\text{signal from unknown}}{\text{signal from mixture}}$$

Standard addition equation:

$$\frac{[X]_i}{[X]_f + [S]_f} = \frac{I_X}{I_{S+X}}$$

Quantitation – *Internal Standard*

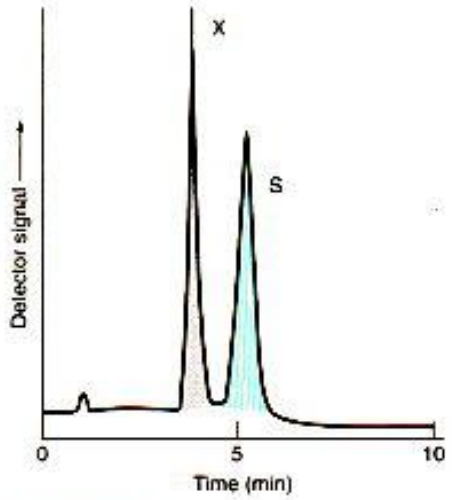


Figure 5-8 Chromatogram illustrating the use of an internal standard. A known amount of standard S is added to unknown X. From the areas of the peaks, we can tell how much X is in the unknown. To do so, we needed to measure the relative response to known amounts of each compound in a separate experiment.

Internal standard:

$$\frac{\text{area of analyte signal}}{\text{concentration of analyte}} = F\left(\frac{\text{area of standard signal}}{\text{concentration of standard}}\right)$$

$$\frac{A_X}{[X]} = F\left(\frac{A_S}{[S]}\right)$$

Internal standard is a known amount of compound, different from the analyte, that is added to an unknown sample.

Signal from analyte is compared with signal for standard to quantify analyte.

Useful when quantity of sample or instrument response varies from run-to-run uncontrollably. Also useful when sample loss occurs during prep.