Chemical Software and Data Analysis

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Seventh Week (05)

Calibration

Calibration

Is a procedure by which an instrument or measuring device is tested in order to determine what its response is for an analyte in a test sample for which the true response is either already known or needs to be established.

When calibrating a spectrophotometer, one measures the instrument's response for a series of known test samples, all of a different concentration, and plots the response vs. concentration (a so called calibration curve or standard curve)

Standardization of Analytical Methods

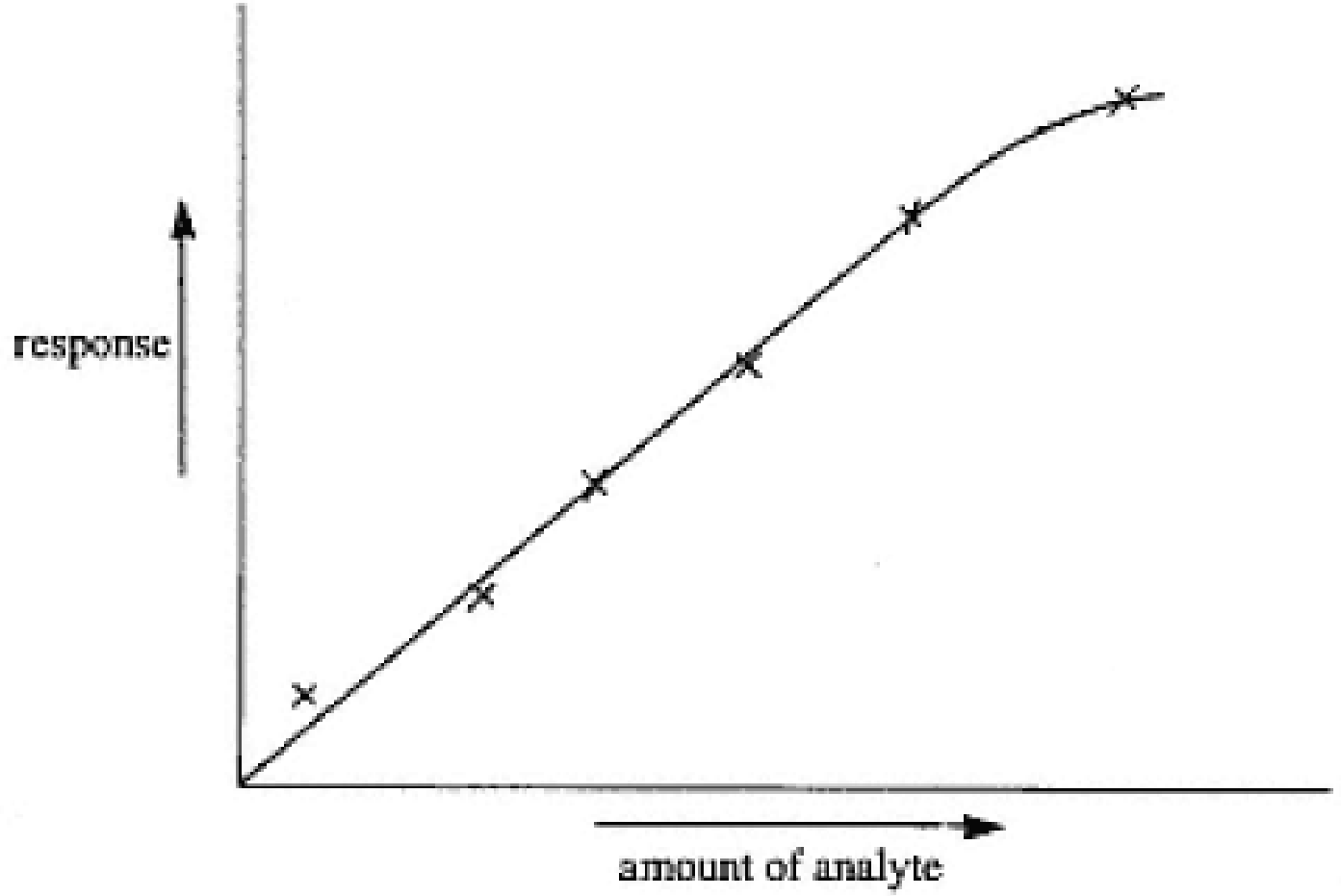
In analytical chemistry, a calibration curve is a general method for determining the concentration of a substance in an unknown sample by comparing the unknown to a set of standard samples of known concentration.

Purpose: To determine specific analyte concentration (amount) from signal, detector response, intensity, A, etc.

Step 1: Measure response to a set of known concentrations ⇨ equation or plot

Step 2: Measure response to sample ⇨ concentration (amount) from plot or eqn

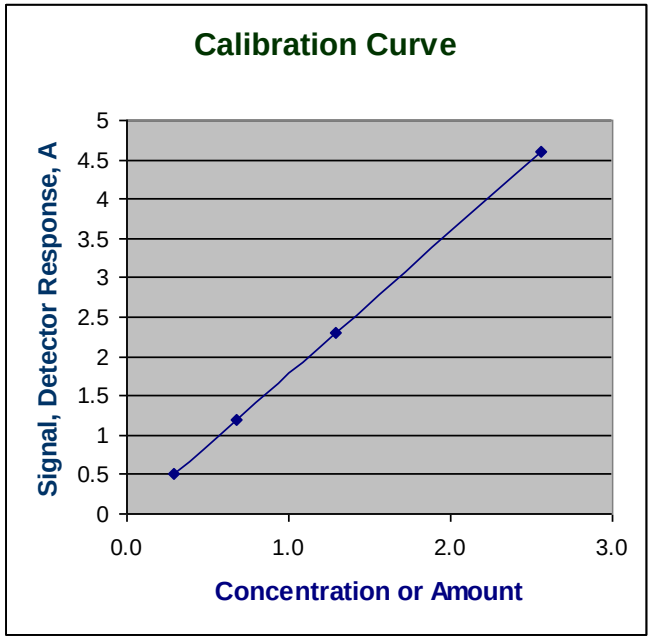
Typical Calibration Curve



Calibration Process

- Standards prepared by serial dilution
- For each analyte of interest
- Multiple measurements (either a different concentration or at selected concentrations)
- Blank (typically reagents alone) can give a “blank correction”

- Range: lowest concentration to highest concentration (validity)
- Linear Range: data fit by y = mx + b



Summary of Process

1. Prepare standard solutions and blank
2. Measure response to standards (corrected for blank)
3. Prepare/calculate graph/equation
4. Measure response to sample (s)
5. Calculate analyte value and uncertainty

Example

- An analytical chemist is tasked with determining the concentration of lead in samples of drinking water. The chemist first makes up standard lead solutions at known concentrations of 0.1 ppm, 0.5 ppm, 1 ppm, 2 ppm, and 5 ppm by diluting a stock lead solution. The chemist then measures the absorbance of each standard solution at a wavelength of 283 nm using a spectrophotometer. The absorbance values obtained are:
- Lead Concentration (ppm) - Absorbance
- Find the concentration for the sample and give us 0.74 absorbance

0.1 ppm	0.05
0.5 ppm	0.22
1 ppm	0.43
2	0.85
5	2.15

New Microsoft Excel Worksheet - Excel

Diyar Ali

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	A	B
14	0.1	0.05
15	0.5	0.22
16	1	0.43
17	2	0.85
18	5	2.15

Sheet1

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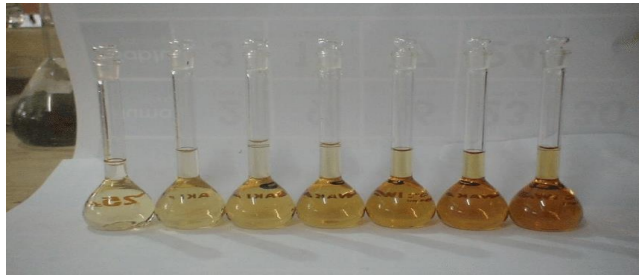
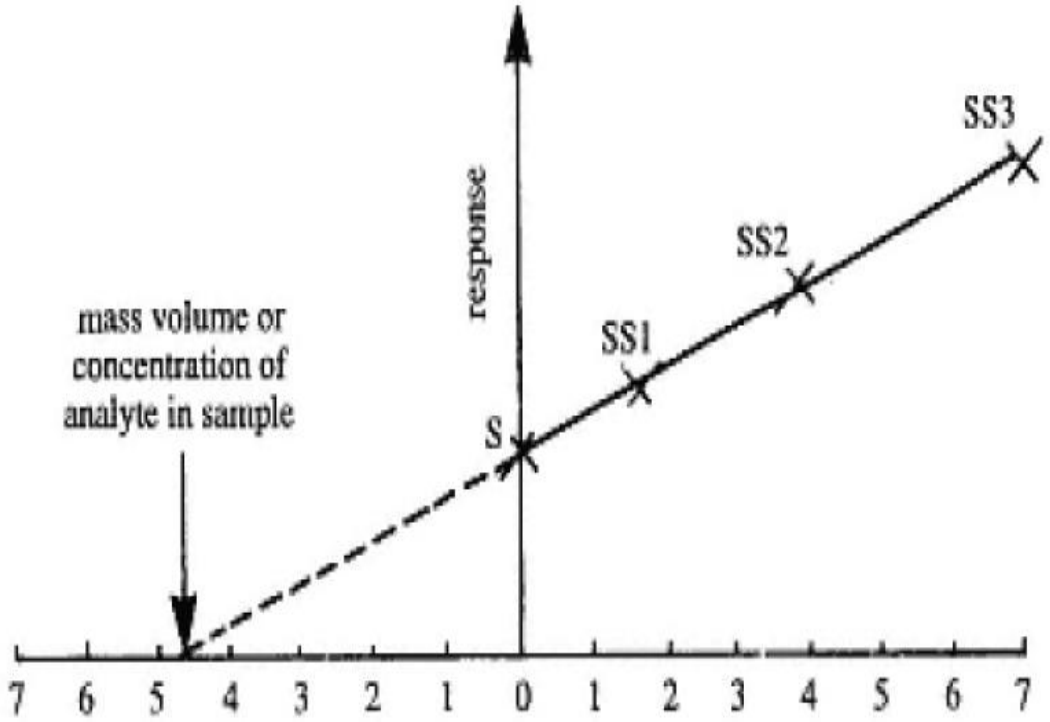
Standardization of Analytical Methods

The method of standard addition is often effective. This involves 'spiking' at least three equal aliquots of the sample with different amounts of the analyte, and then measuring the response for both spiked and unspiked aliquots. A plot of response vs analyte, will give intercepts from which the amount of analyte in the sample may be deduced.



Standard Addition



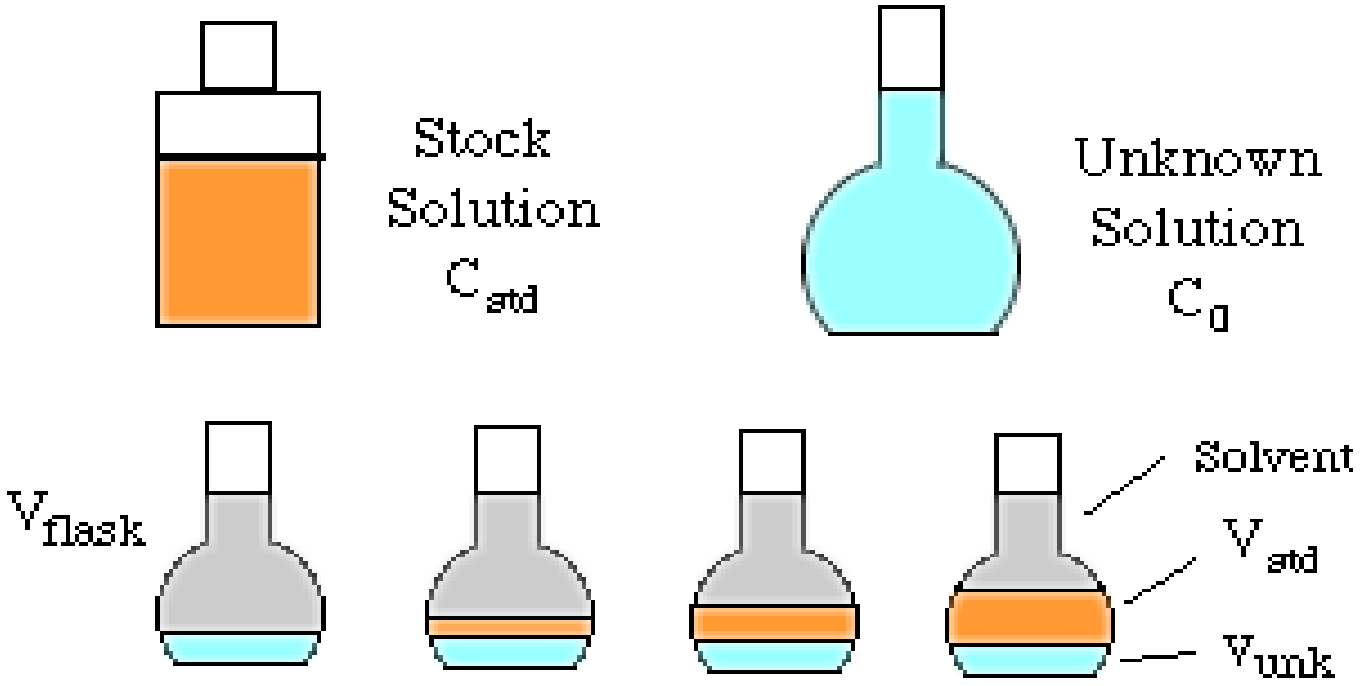
A typical Calibration curve for standard addition; S = unspiked sample; SS1, SS2, SS3 = spiked samples.

Standard Addition

Standard addition must be used whenever the matrix of a sample changes the analytical sensitivity of the method. In other words, the slope of the working curve for standards made with distilled water is different from the same working curve made up in swamp water

Standard Addition

To do constant volume standard addition we need the following solutions and glassware.



Variables

C_o = concentration of unknown in original sample

C_{std} = concentration of stock solution

C_{unk} = concentration of analyte in any given flask

V_{flask} = volume of flask

V_{unk} = volume of unknown added to each flask

V_{std} = volume of stock standard added

$C_{sa} = C_{std}V_{std}/V_{flask}$

Standard Addition

The actual concentration of the analyte in any given flask will be given by:

$$C_{unk} = \frac{C_o V_{unk} + C_{std} V_{std}}{V_{flask}} = \frac{C_o V_{unk}}{V_{flask}} + \frac{C_{std} V_{std}}{V_{flask}}$$

The instrumental response to the analyte will be R = (K) (concentration), so

$$R = K\frac{C_o V_{unk}}{V_{flask}} + K\frac{C_{std} V_{std}}{V_{flask}}$$

Standard Addition

- Now set

$$C_{Sa} = \frac{C_{std} x V_{std}}{V_{flask}}.$$

$$R = K\frac{C_o V_{unk}}{V_{flask}} + KC_{SA}; \quad C_{SA} = \frac{C_{std} V_{std}}{V_{flask}}$$

$$y = b + mx$$

Standard Addition

After measuring the response for a series of standard additions, we plot the results, then extrapolate to y = 0 to get the value of that Csa would need to be to equal the response of the unknown. We use this negative value to compute Co.

Standard Addition

$$0 = K\frac{C_O V_{unk}}{V_{flask}} + KC_{SA}$$

$$C_O = -C_{SA}\frac{V_{flask}}{V_{unk}}$$

Example

- *Another spectrophotometric method to determine Pb^{2+} in blood requires a standard addition calibration curve. Standards were prepared by adding 1.00 ml of blood to each one, and an external standard of 1560 ppb of Pb^{2+} was added. All the samples were diluted to 5.00 ml before measuring the signal. A calibration curve of signal vs volume of standard added produced an equation of:*

$$Signal = 0.266 + 312\, mL^{-1} \times V_{std}$$

What is the concentration of Pb^{2+} in the blood sample?