Calibration Lecture Notes

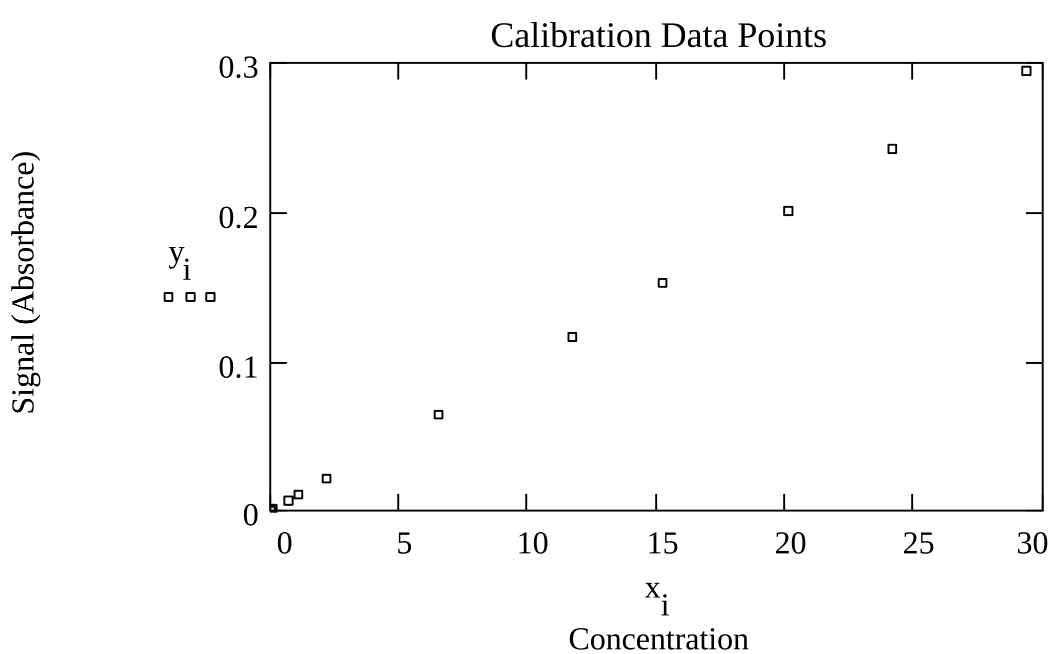
Calibration With Standards

Signal from Standards:

$N := 11 \quad i := 1, 2 .. N$

$x_i :=$ $y_i :=$

x_i	y_i
0	$2.2152 \cdot 10^{-4}$
0.05	$6.785 \cdot 10^{-4}$
0.7	0.00642
1.1	0.01057
2.2	0.02204
6.5	0.06488
11.7	0.11676
15.2	0.15202
20.1	0.20115
24.2	0.24206
29.4	0.29400



Regression Analysis:

$$x_{avg} := \sum_i \frac{x_i}{N} \qquad x_{avg} = 10.10455$$

$$y_{avg} := \sum_i \frac{y_i}{N} \qquad y_{avg} = 0.10098$$

$$s_{xy} := \sum_i \left(x_i \cdot y_i\right) - \left[\frac{\left(\sum_i x_i\right)\cdot\left(\sum_i y_i\right)}{N}\right] \qquad s_{xy} = 11.48360$$

$$s_{yy} := \sum_i \left(y_i\right)^2 - \left[\frac{\left(\sum_i y_i\right)\cdot\left(\sum_i y_i\right)}{N}\right] \qquad s_{yy} = 0.11491$$

$$s_{xx} := \sum_i \left(x_i\right)^2 - \left[\frac{\left(\sum_i x_i\right)\cdot\left(\sum_i x_i\right)}{N}\right] \qquad s_{xx} = 1.14761\cdot 10^3$$

Calculation of line:

Slope:

$$m := \frac{s_{xy}}{s_{xx}} \qquad m = 0.01001$$

Intercept:

$$b := y_{avg} - \left(m \cdot x_{avg}\right) \qquad b = -1.29441\cdot 10^{-4}$$

$$y_{calc_i} := m\cdot\left(x_i\right) + b$$

Uncertainty Calculations:

In the regression

$$s_r := \sqrt{\frac{s_{yy} - \left(m^2 \cdot s_{xx}\right)}{N - 2}} \qquad s_r = 2.60153 \cdot 10^{-4}$$

In the slope

$$s_m := \sqrt{\frac{s_r^{\,2}}{s_{xx}}} \qquad s_m = 7.67947 \cdot 10^{-6}$$

In the intercept

$$s_b := s_r \cdot \sqrt{\frac{\sum_i \left(x_i\right)^2}{N \cdot \sum_i \left(x_i\right)^2 - \left(\sum_i x_i\right)^2}} \qquad s_b = 1.10336 \cdot 10^{-4}$$

Analyisis of an Unknown:

$j := 1 .. 5$ $\qquad M := 5$

$signal_j :=$

0.04247
0.04251
0.04242
0.04262
0.04258

$$signal_{avg} := \sum_j \frac{signal_j}{M}$$

$$signal_{avg} = 0.04252$$

Calculation of unknown

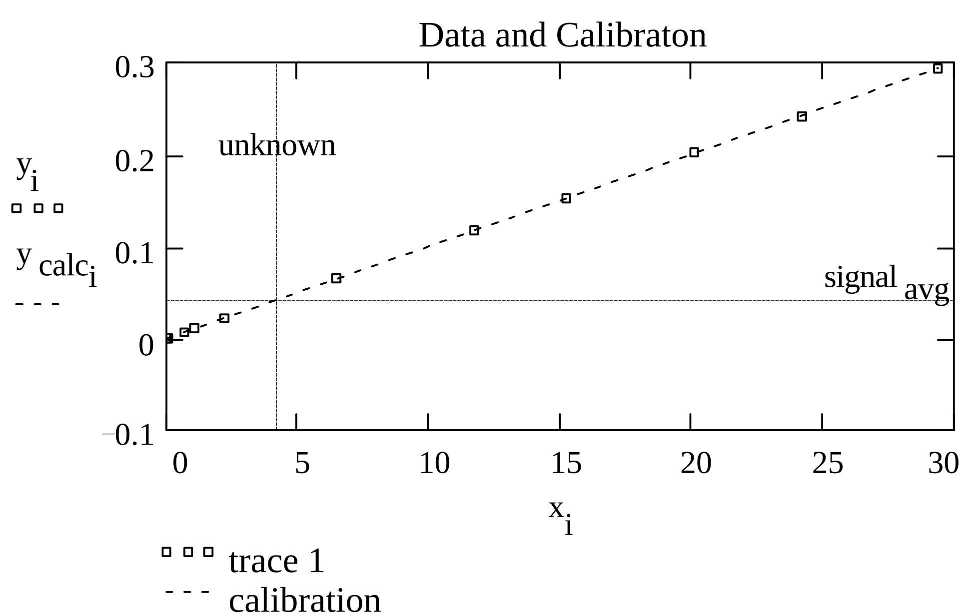
$$unknown := \frac{signal_{avg} - b}{m} \qquad unknown = 4.26217$$

Calculation of uncertainty in unknown

$$s_{unknown} := \left[\left(\frac{s_r}{m} \right) \cdot \sqrt{\frac{1}{M} + \frac{1}{N} + \frac{\left(signal_{avg} - y_{avg} \right)^2}{m^2 \cdot s_{xx}}} \right]$$

$$s_{unknown} = 0.01472$$

$$RSD := \frac{s_{unknown}}{unknown} \qquad RSD = 0.34541 \cdot \%$$



Calibration by Standard Addition (M&M's example):

Mass of the M&M's in the bag:

$$Mass_{initial} := 50 \cdot gm$$

Next you add 5 M&M's to the bag and find the new mass:

$$MM_{added} := 5$$

$$Mass_{final} := 55 \cdot gm$$

mass of the 5 M&M's that you added:

$$Mass_{added} := Mass_{final} - Mass_{initial}$$

$$Mass_{added} = 5.00000 \cdot gm$$

From number of M&M's added, determine mass of each M&M

$$Mass_{MM} := \frac{Mass_{added}}{MM_{added}}$$

$$Mass_{MM} = 1.00000 \cdot gm$$

The number of M&M's initially in the bag

$$MM_{initial} := \frac{Mass_{initial}}{Mass_{MM}}$$

$$MM_{initial} = 50.00000$$

And now it is time to eat!!!

Standard Addition (Chemistry Problem)

Analysis an sample of dirt to determine the concentration of lead

$Signal_{sample} := 0.5879$

$ppm := 10^{-6}$

$C_{standard} := 500 \cdot ppm$

$V_{standard} := 0.1 \cdot mL$

Amount of lead added in the spike.

$$mass_{spike} := C_{standard} \cdot V_{standard} \cdot \left(\frac{1 \cdot gm}{1 \cdot mL} \right)$$

$$mass_{spike} = 5.00000 \cdot 10^{-5} \cdot gm$$

Calculate the increse in the concentration of the sample.

$V_{total} := 100.0 \cdot mL$

$$C_{spiked} := \frac{mass_{spike}}{V_{total} \cdot \left(\frac{1 \cdot gm}{1 \cdot mL} \right)}$$

$$C_{spiked} = 5.00000 \cdot 10^{-7}$$

$$C_{spiked} = 0.50000 \cdot ppm$$

Measure the signal of the spiked sample

$Signal_{spiked} := 0.7816$

The signal of the spike:

$$\mathrm{Signal}_{spike} := \mathrm{Signal}_{spiked} - \mathrm{Signal}_{sample}$$

$$\mathrm{Signal}_{spike} = 0.19370$$

Calculate instrument response $\left(\frac{\mathrm{signal}}{\mathrm{concentration}}\right)$

$$\mathrm{Response} := \frac{\mathrm{Signal}_{spike}}{C_{spiked}}$$

$$\mathrm{Response} = 0.38740 \cdot \mathrm{ppm}^{-1}$$

Now, recall the signal of the orignal sample:

$$\mathrm{Signal}_{sample} = 0.58790$$

This corresponds to a sample concentration of:

$$C_{sample} := \frac{\mathrm{Signal}_{sample}}{\mathrm{Response}}$$

$$C_{sample} = 1.51755 \cdot \mathrm{ppm}$$

But we assumed that the signal from the "spiked sample" is equal to the signal from the sample plus the signal from the spike. Or that:

$$Signal_{spiked} = Signal_{sample} + Signal_{spike}$$

However, the sample is slightly diluted by the volume of the spiking solution (0.1 mL in this example).

So "scale" the signal to account for dilution:

$$Signal_{sample\_adjusted} := Signal_{sample} \cdot \left(\frac{V_{total} - V_{standard}}{V_{total}} \right)$$

$$Signal_{sample\_adjusted} = 0.58731$$

Repeat the above calculations with adjusted signal

The signal of the spike:

$$Signal_{spike\_adjusted} := Signal_{spiked} - Signal_{sample\_adjusted}$$

$$Signal_{spike\_adjusted} = 0.19429$$

The response

$$Response\_adjusted := \frac{Signal_{spike\_adjusted}}{C_{spiked}}$$

$$Response\_adjusted = 0.38858 \cdot ppm^{-1}$$

The adjusted response corresponds to a sample concentration of:

$$C_{sample\_true} := \frac{Signal_{sample}}{Response\_adjusted}$$

$$C_{sample\_true} = 1.51296 \cdot ppm$$

sample_true

Calibration with an Internal Standard:

Run #1, standard mixture with known concentration of Alar and decane.

Alar

Concentration $C_{alar\_std} := 2.871 \cdot ppm$

Peak Area $A_{alar\_std} := 6.824 \cdot 10^{4}$

Decane

Concentration $C_{decane\_std} := 5.55 \cdot ppm$

Peak Area $A_{decane\_std} := 7.31 \cdot 10^{10}$

Calculate Response of Detector

Alar

$$Response_{alar} := \frac{A_{alar\_std}}{C_{alar\_std}}$$

$$Response_{alar} = 2.37687 \cdot 10^{4} \cdot ppm^{-1}$$

Decane

$$Response_{decane} := \frac{A_{decane\_std}}{C_{decane\_std}}$$

$$Response_{decane} = 1.31712 \cdot 10^{10} \cdot ppm^{-1}$$

Relative Response

$$Response_{relative} := \frac{Response_{alar}}{Response_{decane}}$$

$$Response_{relative} = 1.80460 \cdot 10^{-6}$$

Run #2, Unknown Alar concentration spiked with a known concentration of decane.

Alar

Concentration C_{alar_unk}

Peak Area $A_{alar\_unk} := 8.367 \cdot 10^{4}$

Decane

Concentration $C_{decane\_unk} := 2.46 \cdot ppm$

Peak Area $A_{decane\_unk} := 3.23 \cdot 10^{12}$

Response to standard (decane)

$$Response_{decane} := \frac{A_{decane\_unk}}{C_{decane\_unk}}$$

$$Response_{decane} = 1.31301 \cdot 10^{12} \cdot ppm^{-1}$$

Response to unknown (from relative response)

$$Response_{relative} = \frac{Response_{alar}}{Response_{decane}}$$

$$Response_{alar} := Response_{relative} \cdot Response_{decane}$$

$$Response_{alar} = 2.36946 \cdot 10^{6} \cdot ppm^{-1}$$

Concentration of unknown

$$Response_{alar} = \frac{A_{alar\_unk}}{C_{alar\_unk}}$$

$$C_{alar\_unk} := \frac{A_{alar\_unk}}{Response_{alar}}$$

$$C_{alar\_unk} = 0.03531 \cdot ppm$$