

Calibration Lecture Notes

Calibration With Standards

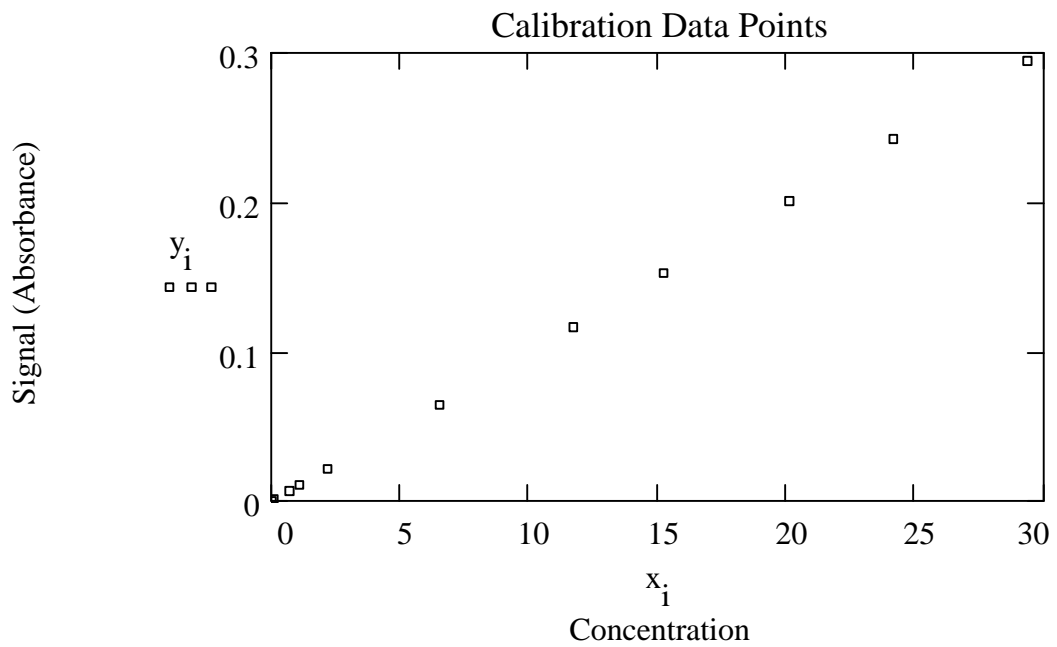
Signal from Standards:

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

$$x_i :=$$

$$y_i :=$$

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



Regression Analysis:

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

$$x_{\text{avg}} = 10.10455$$

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

$$y_{\text{avg}} = 0.10098$$

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

$$s_{xy} = 11.48360$$

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

$$s_{yy} = 0.11491$$

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

$$s_{xx} = 1.14761 \cdot 10^3$$

Calculation of line:

$$\text{Slope: } m := \frac{s_{xy}}{s_{xx}} \quad m = 0.01001$$

Intercept:

$$b := y_{\text{avg}} - (m \cdot x_{\text{avg}}) \quad b = -1.29441 \cdot 10^{-4}$$

$$y_{\text{calc}_i} := m \cdot (x_i) + b$$

Uncertainty Calculations:

In the regression

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

In the slope

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

In the intercept

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

Analysis of an Unknown:

$j := 1..5$

$M := 5$

signal_j :=

0.04247
0.04251
0.04242
0.04262
0.04258

$$\text{signal}_{\text{avg}} := \sum_j \frac{\text{signal}_j}{M}$$

signal_{avg} = 0.04252

Calculation of unknown

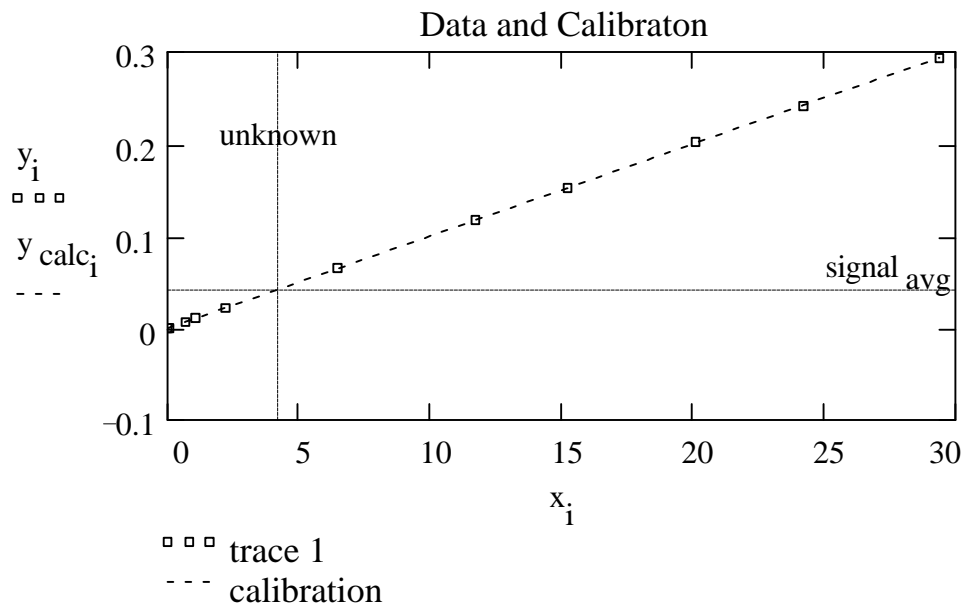
$$\text{unknown} := \frac{\text{signal}_{\text{avg}} - b}{m} \quad \text{unknown} = 4.26217$$

Calculation of uncertainty in unknown

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

$$s_{\text{unknown}} = 0.01472$$

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



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

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

$$\text{Mass}_{\text{initial}} := 50 \cdot \text{gm}$$

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

$$\text{MM}_{\text{added}} := 5$$

$$\text{Mass}_{\text{final}} := 55 \cdot \text{gm}$$

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

$$\text{Mass}_{\text{added}} := \text{Mass}_{\text{final}} - \text{Mass}_{\text{initial}}$$

$$\text{Mass}_{\text{added}} = 5.00000 \cdot \text{gm}$$

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

$$\text{Mass}_{\text{MM}} := \frac{\text{Mass}_{\text{added}}}{\text{MM}_{\text{added}}}$$

$$\text{Mass}_{\text{MM}} = 1.00000 \cdot \text{gm}$$

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

$$\text{MM}_{\text{initial}} := \frac{\text{Mass}_{\text{initial}}}{\text{Mass}_{\text{MM}}}$$

$$\text{MM}_{\text{initial}} = 50.00000$$

And now it is time to eat!!!

Standard Addition (Chemistry Problem)

Analysis an sample of dirt to determine the concentration of lead

$$\text{Signal}_{\text{sample}} := 0.5879 \quad \text{ppm} := 10^{-6}$$

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

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

Amount of lead added in the spike.

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

$$\text{mass}_{\text{spike}} = 5.00000 \cdot 10^{-5} \cdot \text{gm}$$

Calculate the increase in the concentration of the sample.

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

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

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

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

Measure the signal of the spiked sample

$$\text{Signal}_{\text{spiked}} := 0.7816$$

The signal of the spike:

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

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

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

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

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

Now, recall the signal of the original sample:

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

This corresponds to a sample concentration of:

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

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

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:

$$\text{Signal}_{\text{spiked}} = \text{Signal}_{\text{sample}} + \text{Signal}_{\text{spike}}$$

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:

$$\text{Signal}_{\text{sample_adjusted}} := \text{Signal}_{\text{sample}} \cdot \left(\frac{V_{\text{total}} - V_{\text{standard}}}{V_{\text{total}}} \right)$$

$$\text{Signal}_{\text{sample_adjusted}} = 0.58731$$

Repeat the above calculations with adjusted signal

The signal of the spike:

$$\text{Signal}_{\text{spike_adjusted}} := \text{Signal}_{\text{spiked}} - \text{Signal}_{\text{sample_adjusted}}$$

$$\text{Signal}_{\text{spike_adjusted}} = 0.19429$$

The response

$$\text{Response_adjusted} := \frac{\text{Signal}_{\text{spike_adjusted}}}{C_{\text{spiked}}}$$

$$\text{Response_adjusted} = 0.38858 \cdot \text{ppm}^{-1}$$

The adjusted response corresponds to a sample concentration of:

$$C_{\text{sample_true}} := \frac{\text{Signal}_{\text{sample}}}{\text{Response_adjusted}}$$

$$C_{\text{sample_true}} = 1.51296 \cdot \text{ppm}$$

Calibration with an Internal Standard:

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

Alar

$$\text{Concentration} \quad C_{\text{alar_std}} := 2.871 \cdot \text{ppm}$$

$$\text{Peak Area} \quad A_{\text{alar_std}} := 6.824 \cdot 10^4$$

Decane

$$\text{Concentration} \quad C_{\text{decane_std}} := 5.55 \cdot \text{ppm}$$

$$\text{Peak Area} \quad A_{\text{decane_std}} := 7.31 \cdot 10^{10}$$

Calculate Response of Detector

Alar

$$\text{Response}_{\text{alar}} := \frac{A_{\text{alar_std}}}{C_{\text{alar_std}}}$$

$$\text{Response}_{\text{alar}} = 2.37687 \cdot 10^4 \cdot \text{ppm}^{-1}$$

Decane

$$\text{Response}_{\text{decane}} := \frac{A_{\text{decane_std}}}{C_{\text{decane_std}}}$$

$$\text{Response}_{\text{decane}} = 1.31712 \cdot 10^{10} \cdot \text{ppm}^{-1}$$

Relative Response

$$\text{Response}_{\text{relative}} := \frac{\text{Response}_{\text{alar}}}{\text{Response}_{\text{decane}}}$$

$$\text{Response}_{\text{relative}} = 1.80460 \cdot 10^{-6}$$

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

Alar

Concentration $C_{\text{alar_unk}}$

Peak Area $A_{\text{alar_unk}} := 8.367 \cdot 10^4$

Decane

Concentration $C_{\text{decane_unk}} := 2.46 \cdot \text{ppm}$

Peak Area $A_{\text{decane_unk}} := 3.23 \cdot 10^{12}$

Response to standard (decane)

$$\text{Response}_{\text{decane}} := \frac{A_{\text{decane_unk}}}{C_{\text{decane_unk}}}$$

$$\text{Response}_{\text{decane}} = 1.31301 \cdot 10^{12} \cdot \text{ppm}^{-1}$$

Response to unknown (from relative response)

$$\text{Response}_{\text{relative}} = \frac{\text{Response}_{\text{alar}}}{\text{Response}_{\text{decane}}}$$

$$\text{Response}_{\text{alar}} := \text{Response}_{\text{relative}} \cdot \text{Response}_{\text{decane}}$$

$$\text{Response}_{\text{alar}} = 2.36946 \cdot 10^6 \cdot \text{ppm}^{-1}$$

Concentration of unknown

$$\text{Response}_{\text{alar}} = \frac{A_{\text{alar_unk}}}{C_{\text{alar_unk}}}$$

$$C_{\text{alar_unk}} := \frac{A_{\text{alar_unk}}}{\text{Response}_{\text{alar}}}$$

$$C_{\text{alar_unk}} = 0.03531 \cdot \text{ppm}$$