Calibration Example Problems

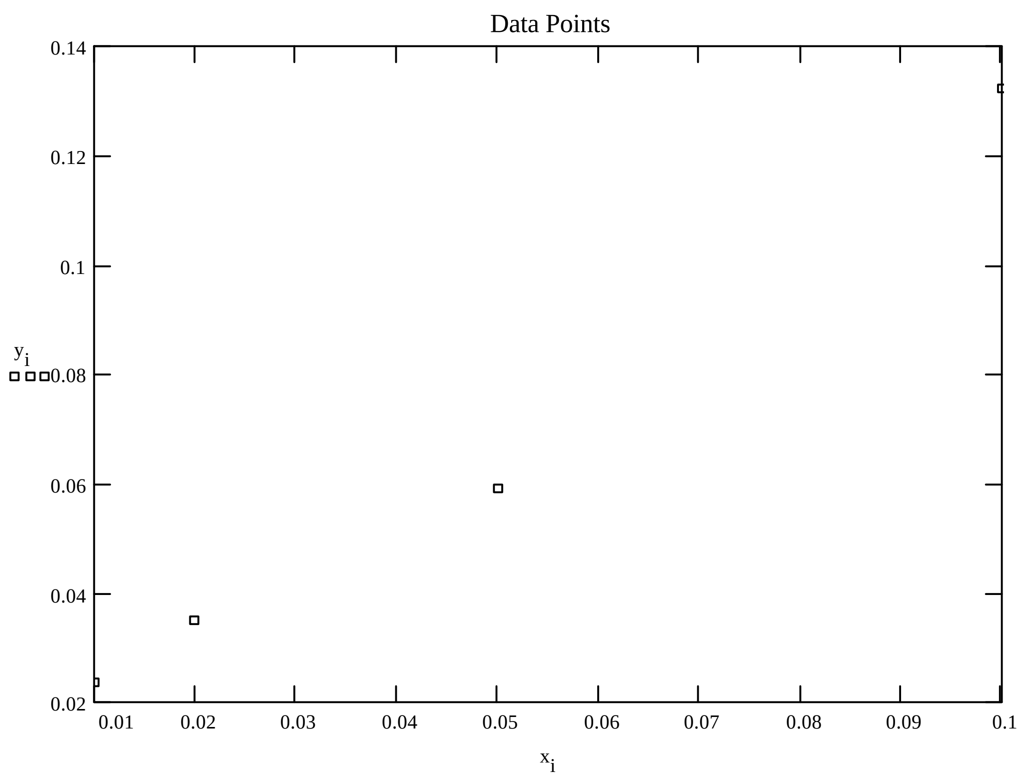
This document document provides an example of calibration calculations and error propagation. It preforms a linear regression analysis on the x, y data set. In addition to the slope and intercept, the regression, slope, and intercept are calculated. At the end of this document is a section for applying the regression analysis to unknowns.

Data Set

$N := 4$

$i := 1, 2 .. N$

$x_i :=$	$y_i :=$	$x_i \cdot y_i$	$(y_i)^2$	$(x_i)^2$
0.01	0.02368	$2.368 \cdot 10^{-4}$	$5.60742 \cdot 10^{-4}$	$1 \cdot 10^{-4}$
0.02	0.03507	$7.014 \cdot 10^{-4}$	0.00123	$4 \cdot 10^{-4}$
0.05	0.05909	0.00295	0.00349	0.0025
0.10	0.13227	0.01323	0.0175	0.01



Regression Analysis:

$$x_{avg} := \sum_i \frac{x_i}{N}$$ $x_{avg} = 0.045$

$$y_{avg} := \sum_i \frac{y_i}{N}$$ $y_{avg} = 0.06253$

$$s_{xy} := \sum_i \left(x_i \cdot y_i\right) - \left[\frac{\left(\sum_i x_i\right)\cdot\left(\sum_i y_i\right)}{N}\right]$$ $s_{xy} = 0.00586$

$$s_{yy} := \sum_i \left(y_i\right)^2 - \left[\frac{\left(\sum_i y_i\right)\cdot\left(\sum_i y_i\right)}{N}\right]$$ $s_{yy} = 0.00714$

$$s_{xx} := \sum_i \left(x_i\right)^2 - \left[\frac{\left(\sum_i x_i\right)\cdot\left(\sum_i x_i\right)}{N}\right]$$ $s_{xx} = 0.0049$

Calculation of line:

Slope:

$$m := \frac{s_{xy}}{s_{xx}}$$ $m = 1.19689$

Intercept:

$$b := y_{avg} - \left(m \cdot x_{avg}\right)$$ $b = 0.00867$

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

Uncertainty Calculations:

In the regression

$$s_r := \sqrt{\frac{s_{yy} - \left(m^2 \cdot s_{xx}\right)}{N-2}} \qquad s_r = 0.00773$$

In the slope

$$s_m := \sqrt{\frac{s_r^{\ 2}}{s_{xx}}} \qquad s_m = 0.11039$$

In the intercept

$$s_b := s_r \cdot \sqrt{\frac{\sum_i \left(x_i\right)^2}{N \cdot \sum_i \left(x_i\right)^2 - \left(\sum_i x_i\right)^2}} \qquad s_b = 0.00629$$

Analyisis of an Unknown:

replicates $\quad M := 1 \quad j := 1, 2 .. M$

$$signal_j := 0.07852 - 0.00597 \qquad signal_{avg} := \sum_j \frac{signal_j}{M}$$

$$ppm := 10^{-6}$$

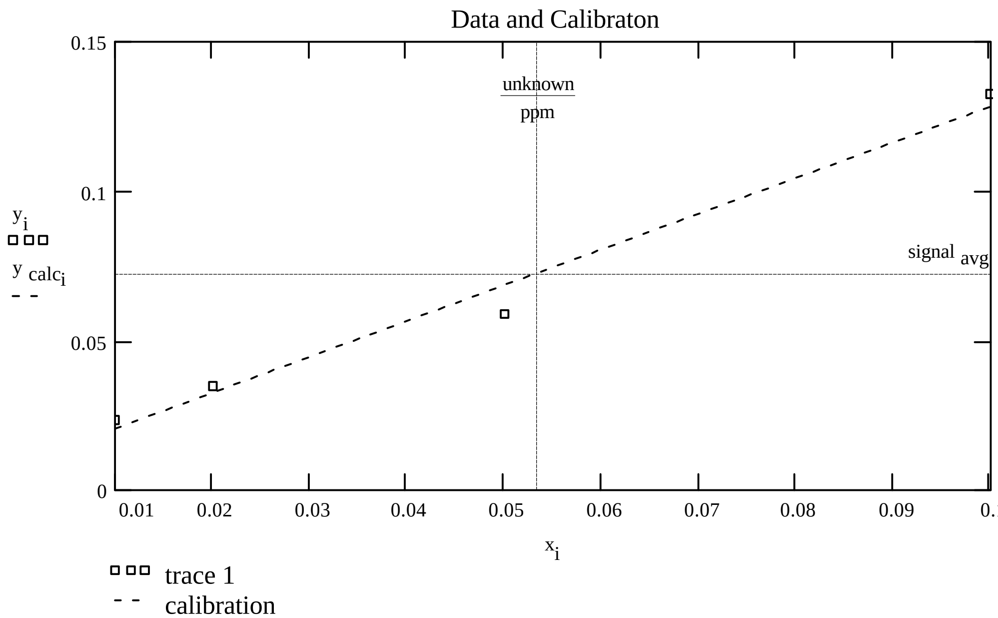
Calculation of unknown

$$unknown := \frac{signal_{avg} - b}{m} \cdot ppm \qquad unknown = 0.05337 \cdot ppm$$

Calculation of uncertainty in unknown

$$s_{unknown} := \left(\frac{s_r}{m}\right) \cdot \sqrt{\frac{1}{M} + \frac{1}{N} + \frac{\left(signal_{avg} - y_{avg}\right)^2}{m^2 \cdot s_{xx}}} \cdot ppm \qquad s_{unknown} = 0.00726 \cdot ppm$$

$$RSD := \frac{s_{unknown}}{unknown} \qquad RSD = 13.60138 \cdot \%$$



Now that the concentration of the unknown solution and the uncertainty in the concentration of the unknown solution has been determined. Let's look at the error propagation. Suppose that the solution that was analyzed was prepared as follows.

5.0456 g of sample was digested with 15 mL of HF
The HF solution was diluted to 100.00 mL in a class A volumetric flask.
10.00 mL of the solution was pipeted with a 10.00 mL class A pipet
This was diluted to 50.00 mL in a class A volumetric flask.

First let's look at the calculations required to determine the concentration of Pb in the original soil sample.

The concentration of the solution is:

$$\text{unknown} = 0.05337 \cdot \text{ppm}$$

The amount of Pb in the solution (assuming a density of 1) is:

$$\text{unknown} \cdot 50.00 \cdot \text{gm} = 2.66869 \cdot 10^{-6} \cdot \text{gm}$$

Mathcad includes calculation that ppm = 10^{-6} with the units.

The concentration of the solution in the pipet (assuming a density of 1) is:

$$\frac{\text{unknown} \cdot 50.00 \cdot \text{gm}}{10 \cdot \text{gm}} = 0.26687 \cdot \text{ppm}$$

NOTE: Even if the density of the solution is not 1, the effect cancels in this step.

The concentration of the solution in the 100.00 mL flask is the same as the concentration of the solution in the pipet.

The amount of Pb in the soluition (assuming a density of 1) is:

$$\text{unknown}\cdot 50\cdot \text{gm}\cdot\left(\frac{1}{10\cdot\text{gm}}\right)\cdot 100\cdot\text{gm} = 2.66869\cdot 10^{-5}\ \cdot\text{gm}$$

The concentration fo Pb in the original soil sample is:

$$\text{unknown}\cdot 50\cdot \text{gm}\cdot\left(\frac{1}{10\cdot\text{gm}}\right)\cdot 100\cdot\text{gm}\cdot\left(\frac{1}{5.0456\cdot\text{gm}}\right) = 5.28914\ \cdot\text{ppm}$$

Since the calculation involves multiplication and division, the error is propagated as follows.

$$s_x = x\cdot\sqrt{\left(\frac{s_a}{a}\right)^2 + \left(\frac{s_b}{b}\right)^2 + \left(\frac{s_c}{c}\right)^2 + \ldots\ldots}$$

The values and their uncertainties (NOTE, this is an example, you need to look up the uncertainty for the glassware) are:

$\text{unknown} = 0.05337\ \cdot\text{ppm}$ $\quad s_{\text{unknown}} = 0.00726\ \cdot\text{ppm}$

$\text{flask}_1 := 50\cdot\text{mL}$ $\quad s_{\text{flask\_1}} := 0.05\cdot\text{mL}$

$\text{pipet} := 10\cdot\text{mL}$ $\quad s_{\text{pipet}} := 0.01\cdot\text{mL}$

$\text{flask}_2 := 100\cdot\text{mL}$ $\quad s_{\text{flask\_2}} := 0.08\cdot\text{mL}$

$\text{sample} := 5.0456\cdot\text{gm}$ $\quad s_{\text{sample}} := 0.0001\cdot\text{gm}$

$$s_x := 5.28914\cdot\text{ppm}\cdot\sqrt{\left(\frac{s_{\text{unknown}}}{\text{unknown}}\right)^2 + \left(\frac{s_{\text{flask\_1}}}{\text{flask}_1}\right)^2 + \left(\frac{s_{\text{pipet}}}{\text{pipet}}\right)^2 + \left(\frac{s_{\text{flask\_2}}}{\text{flask}_2}\right)^2 + \left(\frac{s_{\text{sample}}}{\text{sample}}\right)^2}$$

$$s_x = 0.71943\ \cdot\text{ppm}$$

Or the same calculation showing the numbers:

$$5.29\cdot\text{ppm}\cdot\sqrt{\left(\frac{0.00726}{0.05337}\right)^2 + \left(\frac{0.05}{50}\right)^2 + \left(\frac{0.01}{10}\right)^2 + \left(\frac{0.08}{100}\right)^2 + \left(\frac{0.0001}{5.0456}\right)^2} = 0.71966\ \cdot\text{ppm}$$

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