Example - Internal Standards

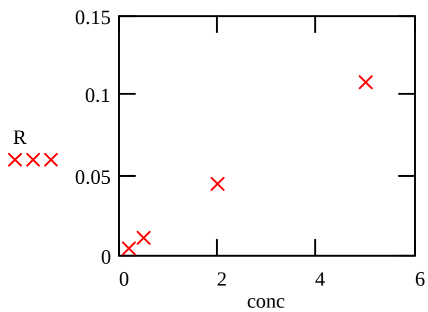
$conc := (0.2 \;\; 0.5 \;\; 2.0 \;\; 5.0)^T$ Na concs, in ppm

$S_{Na} := (0.22 \;\; 0.53 \;\; 2.30 \;\; 5.00)^T$ Na emission signal

$S_{Li} := (48 \;\; 47 \;\; 51 \;\; 46)^T$ Li emission signal

$unk_{Na} := 0.88$ $\quad unk_{Li} := 48$ emission signals for the "unknown" sample

$i := 0 .. 3$ $\quad R_i := \frac{S_{Na_i}}{S_{Li_i}}$ $\quad R^T = \left[\, 4.5833 \cdot 10^{-3} \quad 0.0113 \quad 0.0451 \quad 0.1087 \,\right]$ define a new variable



Looks linear. Let's calculate LS estimates.

$b_0 := \text{intercept}(conc, R)$ $\quad b_0 = 6.8064 \cdot 10^{-4}$

$b_1 := \text{slope}(conc, R)$ $\quad b_1 = 0.0217$

$S_{xx} := 3 \cdot \text{Var}(conc)$ $\quad xbar := \text{mean}(conc)$

point estimate $\quad R_{unk} := \frac{unk_{Na}}{unk_{Li}}$ $\quad R_{unk} = 0.0183$ $\quad conc_{unk} := \frac{R_{unk} - b_0}{b_1}$ $\quad conc_{unk} = 0.8143$

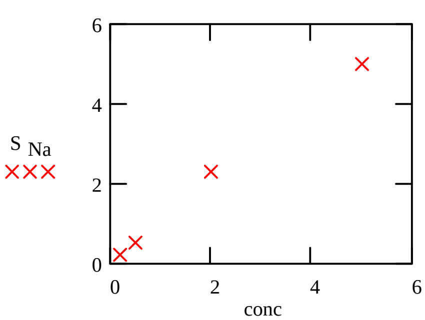
std error $\quad fit := b_1 \cdot conc + b_0$ $\quad res := R - fit$ $\quad s_{res} := \sqrt{\frac{1}{2} \cdot \sum \overrightarrow{res^2}}$ $\quad s_{res} = 8.6995 \cdot 10^{-4}$

$se_{unk} := \frac{s_{res}}{b_1} \cdot \sqrt{1 + \frac{1}{4} + \frac{(conc_{unk} - xbar)^2}{S_{xx}}}$ $\quad se_{unk} = 0.0464$

Now for the confidence interval: $\quad t := qt(.975, 2)$ $\quad t = 4.3027$ $\quad t \cdot se_{unk} = 0.1995$

The concentration of sodium in the sample is 0.81 +/- 0.20 ppm (95% CL).

Let's compare this result to that of the calibration curve method (ie, ignoring the measurements of lithium signal).



$b_0 := \text{intercept}(conc, S_{Na})$ $\quad b_1 := \text{slope}(conc, S_{Na})$

$fit := b_1 \cdot conc + b_0$ $\quad res := S_{Na} - fit$

$s_{res} := \sqrt{\frac{1}{2} \cdot \sum \overrightarrow{res^2}}$ $\quad s_{res} = 0.1739$ (larger than previously)

$S_{xx} = 14.4675$ $\quad xbar = 1.9250$

$\frac{unk_{Na} - b_0}{b_1} = 0.7882$ $\quad \frac{s_{res}}{b_1} \cdot \sqrt{1 + \frac{1}{4} + \frac{(0.7882 - xbar)^2}{S_{xx}}} = 0.2020$

Precision is more than four times worse than with the internal standards method.