Example: Standard Additions with Potentiometry

$V_a := 50.00$ volume of sample, in mL $C_{std} := 10.00$ std conc, in mg/mL

slope of calibration curve (E vs logC), in mV/decade. This value is necessary to linearize the std additions plot for potentiometry.

$V_{std} := (0.0\ \ 0.5\ \ 1.0\ \ 1.5\ \ 2.0)^T$ volume of added std, in mL

$E1 := (-632.7\ \ -631.9\ \ -626.6\ \ -625.0\ \ -619.9)^T$

$E2 := (-631.7\ \ -632.6\ \ -624.7\ \ -625.5\ \ -620.3)^T$

$E3 := (-631.1\ \ -631.4\ \ -625.0\ \ -623.1\ \ -620.5)^T$

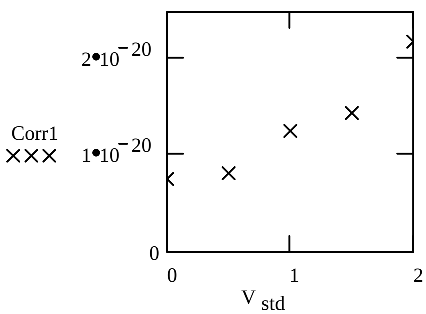
Std additions measurements, in mV, on the three sample portions

Let's apply a correction factor to "linearize" the plot.

$m := 29.0$ slope of calibration curve (E vs logC). This value is needed to linearize.

$i := 0 .. 4$

$Corr1_i := \left(V_a + V_{std_i}\right) \cdot 10^{\frac{E1_i}{m}}$ $Corr2_i := \left(V_a + V_{std_i}\right) \cdot 10^{\frac{E2_i}{m}}$ $Corr3_i := \left(V_a + V_{std_i}\right) \cdot 10^{\frac{E3_i}{m}}$



This is the first standard additions plot. Although a little noisy, it is reasonably linear (potentiometric std addition plots never look very pretty).

Now we can do our calculations.

sample 1 $b_0 := \text{intercept}(V_{std}, Corr1)$ $b_1 := \text{slope}(V_{std}, Corr1)$ $b_0 = 5.9931 \cdot 10^{-21}$ $b_1 = 6.9596 \cdot 10^{-21}$

$Vprime := \frac{b_0}{b_1}$ $Vprime = 0.8611$ in mL

$conc1 := C_{std} \cdot \frac{Vprime}{V_a}$ $conc1 = 0.1722$ concentration in mg/mL

sample 2 $b_0 := \text{intercept}(V_{std}, Corr2)$ $b_1 := \text{slope}(V_{std}, Corr2)$ $b_0 = 6.7409 \cdot 10^{-21}$ $b_1 = 6.4103 \cdot 10^{-21}$

$Vprime := \frac{b_0}{b_1}$ $Vprime = 1.0516$ in mL

$conc2 := C_{std} \cdot \frac{Vprime}{V_a}$ $conc2 = 0.2103$ concentration in mg/mL sample 3 $b_0 := \text{intercept}(V_{std}, \text{Corr3})$ $b_1 := \text{slope}(V_{std}, \text{Corr3})$ $b_0 = 7.2901 \cdot 10^{-21}$ $b_1 = 6.5441 \cdot 10^{-21}$

$\text{Vprime} := \dfrac{b_0}{b_1}$ $\text{Vprime} = 1.1140$ in mL

$\text{conc3} := C_{std} \cdot \dfrac{\text{Vprime}}{V_a}$ $\text{conc3} = 0.2228$ concentration in mg/mL

Now we have three independent point estimates of the same quantity (ie, the concentration of cadmium cations in the seawater. We can calculate a confidence interval in the usual fashion.

$\text{mean}\left((\text{conc1} \;\; \text{conc2} \;\; \text{conc3})^T\right) = 0.2018$ $\text{StdErr} := \dfrac{\text{Stdev}\left((\text{conc1} \;\; \text{conc2} \;\; \text{conc3})^T\right)}{\sqrt{3}}$ $\text{StdErr} = 0.0152$

$t := \text{qt}(.975, 2)$ $t = 4.3027$ $t \cdot \text{StdErr} = 0.0654$ width of 95% CI

The concentration of cadmium in the seawater is 0.202 ± 0.065 mg/mL (95% CL)