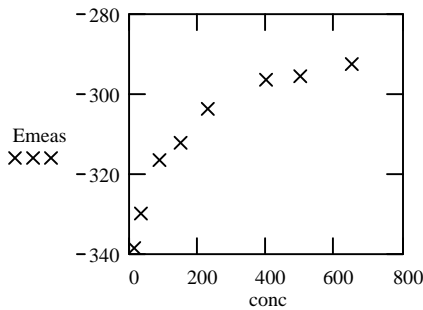


Potentiometry Example

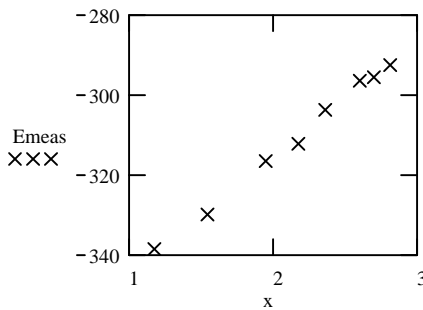
conc := (15 35 89 150 230 400 500 650)^T Emeas := (-338.5 -329.8 -316.5 -312.2 -303.7 -296.4 -295.5 -292.5)^T

Let's look at a plot of the calibration data.



Doesn't look too linear! What's wrong? I forgot that potentiometric measurements are proportional to the **logarithm** of the analyte concentration.

$$x := \log(\text{conc})$$



That's a little better. Let's calculate the least-squares estimates of the slope and intercept of a best-fit line for this data.

$$b_0 := \text{intercept}(x, \text{Emeas}) \quad b_0 = -373.5409$$

$$b_1 := \text{slope}(x, \text{Emeas}) \quad b_1 = 29.0525 \quad (\text{slope is close to theoretical value of } 29.6 \text{ mV/decade})$$

We need to calculate a few things first

$$\text{fit} := b_1 \cdot x + b_0 \quad \text{res} := \text{Emeas} - \text{fit} \quad \text{res}^T = [0.8725 \quad -1.1181 \quad 0.4063 \quad -1.8800 \quad 1.2268 \quad 1.5446 \quad -0.3709 \quad -0.6812]$$

$$s_{\text{res}} := \sqrt{\frac{1}{6} \cdot \sum \text{res}^2} \quad s_{\text{res}} = 1.3041 \quad \text{std dev of residuals (6 df)} \quad S_{xx} := 7 \cdot \text{Var}(x) \quad S_{xx} = 2.3447$$

Now we can use our calibration curve to obtain a point estimate of the analyte concentration

$$y_u := -300.8 \quad \text{signal for "unknown", in mV}$$

$$x_u := \frac{y_u - b_0}{b_1} \quad x_u = 2.5038 \quad \text{conc}_u := 10^{x_u} \quad \text{conc}_u = 318.9887 \quad \text{point estimate of concentration, in ppm}$$

Now we can determine the standard error of our point estimate

$$se_u := \frac{s_{\text{res}}}{b_1} \cdot \sqrt{1 + \frac{1}{8} + \frac{(x_u - \text{mean}(x))^2}{S_{xx}}} \quad se_u = 0.0486 \quad \text{this is the std error of the value calc'd for } x_u$$

In order to determine the standard error of our estimate of the analyte concentration, we must perform propagation of error. [Remember that we took the antilog of x_u to calculate the concentration]

$$\text{RSD}_{\text{conc}} := 2.303 \cdot se_u \quad se_{\text{conc}} := \text{RSD}_{\text{conc}} \cdot \text{conc}_u \quad se_{\text{conc}} = 35.7270 \quad \text{std error of point estimate, in ppm}$$

So we have a point estimate of the concentration - 319.0 ppm - and the standard error of that point estimate - 35.7 ppm. It would appear that we can calculate a confidence interval using these two numbers, as follows.

$$t := qt(.975, 6) \quad t = 2.4469 \quad t \cdot se_{\text{conc}} = 87.4207 \quad 95\% \text{ CI is } 319 \pm 87 \text{ ppm.}$$

There is a problem with this confidence interval, though. It assumes that our point estimate of analyte concentration is normally distributed. However, if the calibration measurements are normally distributed, then it is x_u - the log of the sample concentration - that will be normally distributed. The antilog is nonlinear transformation, and so the distribution of the point estimate of the concentration will be skewed relative to the normal distribution. Thus, strictly speaking, we should not use the confidence interval calculated above.

What to do? We can calculate a confidence interval for x_u and then take the antilog of the upper and lower values of the interval, as follows.

$$x_u = 2.5038 \quad se_u = 0.0486 \quad t \cdot se_u = 0.1190 \quad 95\% \text{ CI is } 2.50 \pm 0.12$$

$$\text{lower} := x_u - t \cdot se_u \quad \text{lower} = 2.3848 \quad 10^{\text{lower}} = 242.5358 \quad \text{lower boundary of 95\% CI}$$

$$\text{upper} := x_u + t \cdot se_u \quad \text{upper} = 2.6228 \quad 10^{\text{upper}} = 419.5414 \quad \text{upper boundary of 95\% CI}$$

Thus, a 95% confidence interval for the analyte concentration is 243 - 420 ppm. The point estimate for the analyte concentration is 319 ppm.

Note that the point estimate is not exactly in the middle of the confidence interval, reflecting the skewed nature of the probability distribution. It is interesting to compare the boundary values of the actual confidence interval with the one calculated previously using the propagation of errors approach.

$$319 - 87 = 232 \quad 319 + 87 = 406 \quad \text{Propagation of error approach gives a 95\% CI of 232-406 ppm, which is slightly different than the "true" CI.}$$

Some people would use the error propagation approach and not worry too much about the non-normal distribution of the point estimate. They would argue that the assumptions of homogeneous and normal distribution of measurement error in the calibration measurements is often violated anyway, so that the propagation of error approach is just as valid as the other. There is some merit to this argument.