14-1  (a) Note that in this question we are not using the calibration curve to find an unknown. rather we are only be asked to characterize the calibration curve. The data comes nicely out of the LINEST function in Excel. The curve is

![Phenathroline Calibration Curve](image)

(b) From LINEST we find the following:

\[ b = 0.01478 \quad m = 0.07812 \]

These are the parameters for the linear fit to the data.

(c) The standard deviation about the regression is the same as the standard deviation of the fit. It is the is the square root of the sum of the square residuals divided by the degrees of freedom, which is \( 6 - 2 = 4 \). The value is 0.01244.

(d) The standard deviation of the slope \( m \) is 0.00082

14-2  In both questions 1 and 2, it is possible that you could become concerned with the dilution steps. Answering the question about what the concentration actually is in a given cuvette would need to account for any dilution. But as long as the calibration curve samples are treated in exactly the same way as the unknown samples, then the dilution effects would cancel and we can compare the known concentrations to the unknown concentrations with the additional arithmetic to find dilution effects. Again, as long as the work up for each sample is the same you can ignore the dilution effects, unless something specific about concentration in a particular measurement is sought.
To find the unknown concentrations, we need just invert the calibration curve’s linear equation, use the measured absorbance (y), and solve for the unknown concentration (x).

(a)  
\[ y = m x + b \]
\[ 0.107 = 0.0781 x + 0.01478 \]
\[ x = \frac{0.107 - 0.01478}{0.07812} = 1.18 \text{ ppm of Fe} \]

We do the same thing for the other two unknowns to find
(b) 9.04 ppm  
(c) 19.50 ppm  

We are also asked to find the standard deviation for each of these measurements. Recall the statistical section we did, which provides an equation for the variance of the unknown. We need to go back and calculate sums, sums of squares, and the determinant from the original data. We have already determined the variance of the fit (the square of the standard deviation about the regression determined in 14-1. We find
\[ \sum x_i = 63 \quad \sum x_i^2 = 893 \]
\[ Det = n \sum x_i^2 - (\sum x_i)^2 = 1389 \]

If we use these data we find the variances for each unknown. The square root is the standard deviation.

The variance equation uses the variable p to consider the effect of multiple samples for the unknown, we first use p=1 and then p=3. We obtain
(a) (x=1.18 ppm) \( \sigma = 0.198 \)  
(b) (x=9.04 ppm) \( \sigma = 0.173 \)  
(c) (x=19.50 ppm) \( \sigma = 0.196 \)

and then with p = 3
(a) (x=1.18 ppm) \( \sigma = 0.149 \)  
(b) (x=9.04 ppm) \( \sigma = 0.114 \)  
(c) (x=19.50 ppm) \( \sigma = 0.147 \)

These standard deviations can then be used to find confidence limits, but that was not requested in this problem.

14-6 For each solution, we need to solve two simultaneous equations to find the concentrations. Since we are given the molar absorptivities, we can proceed directly. The absorbance at any wavelength is a sum of the absorbance of each species individually at that wavelength.

(a)  
\[ A_{365} = 3529 \times 1.0 \times [\text{Co}] + 3228 \times 1.0 \times [\text{Ni}] = 0.598 \]
\[ A_{700} = 428.9 \times 1.0 \times [\text{Co}] + 10.2 \times 1.0 \times [\text{Ni}] = 0.039 \]

Take the equation for absorbance at 365 nm and solve it for concentration of Co. It will still depend upon the as-yet-unknown concentration of Ni.
\[ 0.598 = 3529[\text{Co}] + 3228[\text{Ni}] \]
\[ [\text{Co}] = \frac{0.598 - 3228[\text{Ni}]}{3529} \]
Substitute this into the other absorbance equation and solve for Ni. Now the only unknown is the concentration of Ni so we get a number from this step.

\[ 0.039 = 428.9 \left[ \frac{0.598 - 3228[Ni]}{3529} \right] + 10.2[Ni] \]
\[ 0.039 = 0.07268 - 392.32[Ni] + 10.2[Ni] \]
\[ 0.039 - 0.07268 = -0.0337 = -382.12[Ni] \]

\[ [Ni] = \frac{0.0337}{382.12} = 8.82 \times 10^{-5} \text{ M} \]

Substitute this back into any of the original expressions to solve for the concentration of Co.

\[ [Co] = \frac{0.598 - 322.8 \left( 8.82 \times 10^{-5} \right)}{3529} = 8.88 \times 10^{-5} \text{ M} \]

We do the same thing for the other sample and obtain

\[ [Ni] = 9.8 \times 10^{-5} \text{ M} \quad [Co] = 1.66 \times 10^{-4} \text{ M} \]

14-7 This problem ends up just like the previous questions, except that the we must use the data from the pure samples to determine the value of the molar absorptivities at each wavelength for both species first. This is just a bunch of Beer’s Law stuff.

At 475 nm

\[ A = \varepsilon bc \]
\[ \varepsilon_{475}^A = \frac{A^A}{bc_A} = \frac{0.129}{(1)(8.50 \times 10^{-5})} = 1518 \]
\[ \varepsilon_{475}^B = \frac{A^B}{bc_B} = \frac{0.567}{(1)(4.65 \times 10^{-5})} = 12194 \]

And at 700 nm

\[ \varepsilon_{700}^A = \frac{A^A}{bc_A} = \frac{0.764}{(1)(8.50 \times 10^{-5})} = 8988 \]
\[ \varepsilon_{700}^B = \frac{A^B}{bc_B} = \frac{0.083}{(1)(4.65 \times 10^{-5})} = 1785 \]

Set up the same simultaneous equations again. Watch out: we are using a different cell path length this time.

\[ A_{475} = 1518 \times 1.25 \times [A] + 12194 \times 1.25 \times [B] = 0.502 \]
\[ A_{700} = 8988 \times 1.25 \times [A] + 1785 \times 1.25 \times [B] = 0.912 \]
Solve the first equation for A, substitute into the second and solve for B. Substitute back and get the number for A.

$$0.502 = 1897.5[A] + 15242.5[B]$$

$$[A] = \frac{0.502 - 15242.5[B]}{1897.5}$$

$$0.912 = 11247.5 \left( \frac{0.502 - 15242.5[B]}{1897.5} \right) + 2231.25[B]$$

$$= 2.976 - 90350[B] + 2231.25[B]$$

$$-2.064 = -88119[B]$$

$$[B] = \frac{2.064}{88119} = 2.34 \times 10^{-5} \text{ M}$$

$$[A] = \frac{0.502 - 15242.5(2.34 \times 10^{-5})}{1897.5} = 7.66 \times 10^{-5} \text{ M}$$

The same work for the second mixed sample gives

$$[A] = 5.45 \times 10^{-5} \quad \text{and} \quad [B] = 3.75 \times 10^{-5}$$