Characterizing Uncertainty in Measurements

In this experiment you will prepare several solutions of the primary standard potassium ferricyanide, $K_3[Fe(CN)_6]$ and record the visible spectrum for each solution. You also will record the spectra of several samples prepared for you. Finally, you will use your data and the data of your peers to characterize the uncertainty in your work. You may wish to update your versions of `R` and of `RStudio`, and you will need to download the packages *readr* and *chemCal*.

Preparing Samples and Collecting Spectra

Using the stock solution of nominally 0.01 M $K_3[Fe(CN)_6]$, prepare the following sets of samples, all of which contain the same concentration of $Fe(CN)_6^{3-}$, the species responsible for the solution's color:

- Set One: prepare five samples of nominally 4.0×10^{-4} M $Fe(CN)_6^{3-}$ by diluting 4.00 mL of the stock solution to 100.0 mL using a volumetric pipet and a volumetric flask.
- Set Two: prepare five samples of nominally 4.0×10^{-4} M $Fe(CN)_6^{3-}$ by diluting 2.00 mL of the stock solution to 50.00 mL using a volumetric pipet and a volumetric flask.
- Set Three: prepare five samples of nominally 4.0×10^{-4} M $Fe(CN)_6^{3-}$ by diluting 1.00 mL of the stock solution to 25.00 mL using a volumetric pipet and a volumetric flask.

Obtain and set-up a Vernier spectrometer, using deionized water as a reference. Record the spectrum of each solution in Set One. Be sure to store each spectrum as you collect it (Experiment: Store Latest Run) and to save the full data file for each set when you are done (File: Save) using the filename YourInitials_SetI. Repeat for the solutions in Set Two, and Set Three, using the filename YourInitials_SetII and YourInitials_SetIII.

Using the stock solution of nominally 0.01 M $K_3[Fe(CN)_6]$, prepare the following new set of samples:

- Set Four: prepare a series of solutions by diluting 1.00 mL, 3.00 mL, 5.00 mL, 8.00 mL, and 10.00 mL of the stock solution to 100.0 mL using volumetric glassware.

Record the spectrum of each solution in Set Four. Be sure to store each spectrum as you collect it (Experiment: Store Latest Run) and to save the full data file for each set when you are done (File: Save) using the filename YourInitials_SetIV.

Using the third solution from Set Four (the one prepared by diluting 5.00 mL of the stock solution to 100.0 mL), obtain five spectra, emptying and refilling the cuvette before you collect each spectrum. Be sure to store each spectrum as you collect it (Experiment: Store Latest Run) and to save the full data file for each set when you are done (File: Save) using the filename YourInitials_SetV.

Using the third solution from Set Four (the one prepared by diluting 5.00 mL of the stock solution to 100.0 mL), fill a cuvette and obtain five spectra, leaving the cuvette in place between each spectrum. Be sure to store each spectrum as you collect it (Experiment: Store Latest Run) and to save the full data file for each set when you are done (File: Save) using the filename YourInitials_SetVI.

Record the spectra for the three samples available in lab. Be sure to store each spectrum as you collect it (Experiment: Store Latest Run) and to save the full data file for each set when you are done (File: Save) using the filename YourInitials_SetVII.

Finally, obtain five spectra using deionized water as your sample, emptying and refilling the cuvette each time. Be sure to store each spectrum as you collect it (Experiment: Store Latest Run) and to save the full data file for each set when you are done (File: Save) using the filename YourInitials_SetVIII.

Processing Your Spectra

At this point you should have eight data files, seven with five spectra each and one with three spectra. Export each file and save as a .csv file (File: Export As: CSV...) maintaining the base filename of YourInitials_SetNumber.

Import each .csv file into R as a dataframe, maintaining the base filename of YourInitials_SetNumber. Clean up each file so that it contains just one column of wavelengths (in the first column) and name the column "wavelength." Rename the remaining columns of absorbance values using "a", "b", ... as column names. Be sure to save the dataframe as a .RData file so that it is available to you later. Email a copy of your .RData file for Set I to your peers and to me by the end of the day on Thursday, February 7th.

Analyzing Your Data

Examine your data and determine λ_{max}, which should be close to 420 nm; the absorbance at this wavelength for each spectrum is your data. Answer the following questions in clearly written prose, weaving output from R into your narrative. A **hard copy** of your report is due on February 19th with copies of your .RData files forwarded to me by email. As your work on these questions, you may wish to review material in Sections 4G, 5D, and 14C of *Analytical Chemistry 2.1* and Section 6.2 of Eurochem's *The Fitness for Purpose of Analytical Methods*.

1. Complete an analysis of variance using your data for Sets I–III at λ_{max} and comment on what you learn from this analysis.
2. Complete an analysis of variance using your data and the data from your peers for Set I at λ_{max} and comment on what you learn from this analysis.
3. Complete a linear regression analysis using your data for Set IV at λ_{max} and prepare a plot that includes the data, the regression line, and the confidence and prediction bands; use the package *chemCal* to create your plot. Comment on what you learn from this analysis.
4. Using your data for Set VII, determine the concentration of $K_3[Fe(CN)_6]$ in each sample and its prediction interval. Use the package *chemCal* for this purpose. Comment on what you learn from this analysis.
5. The only difference between Set V and Set VI is whether or not you refilled the cuvette between the recording of spectra. Speculate on why you might find that there is a significant difference between the results for these two sets and then determine if there is any evidence of a significant difference for your data.
6. Using your data for Set VIII and your regression model, determine the limit of detection and the limit of quantification.