Experiment 9: Determination of Iron with 1,10-Phenanthroline

PURPOSE:

This exercise reviews the fundamental concepts of quantitative spectrophotometric analysis.

THEORY:

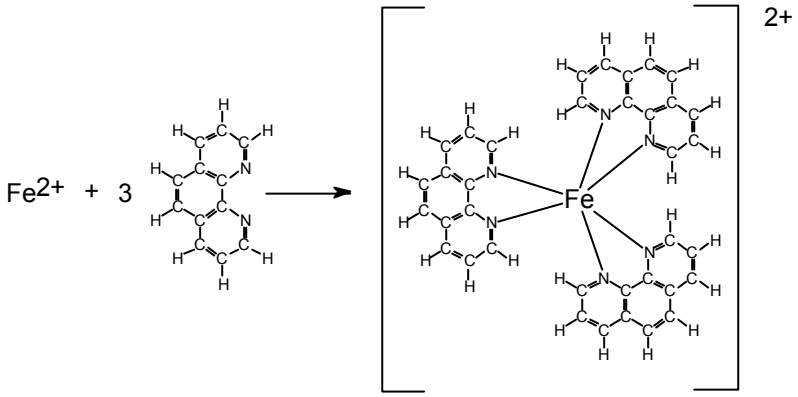
Harris, D. C. (**2003**); **"Quantitative Chemical Analysis 6th ed."**; 258-261, 407-422, first figure @ pp. 453, 461-476, 707-709.

In this experiment, the amount of iron present in a sample is determined by first reacting the iron with 1,10-phenanthroline to form a colored complex and then measuring the amount of light absorbed by this complex. Beer´s law can then be used to determine the concentration relative to absorption: $A = \varepsilon bc$.

To form a complex, the iron must be first reduced to its ferrous state. This reduction is done by reacting the iron with hydroxylamine hydrochloride by the following reaction:

$$2\ Fe^{+3} + 2\ NH_2OH + 2\ OH^- \rightarrow 2\ Fe^{+2} + N_2 + 4\ H_2O$$

Then the reaction with 1,10-phenanthroline is:



Once a colored complex is formed, the wavelength of light which is most strongly absorbed is found by measuring the absorbance at various wavelengths between 400 - 600 nm. After the most suitable wavelength is determined, a series of iron standards is measured at this wavelength and a calibration plot of absorbance vs. concentration is prepared. The absorbance of the unknown sample is measured and the calibration curve is used to calculate the concentration of iron in the sample.

PRELAB EXERCISE (2 pts./e.a.):

Harris, D. C. (**2003**); **"Quantitative Chemical Analysis 6th ed."**: 18-8, 18-9

Also discuss the following:

1. What is a chromophore?
2. Why it is necessary to wait for at least 10 min. before reading the laboratory samples on the spectrophotometer?
3. What is a chelating agent?

EXPERIMENTAL:

NOTE: All iron solutions should be discarded into a "Heavy Metal" waste container.

1. Obtain your unknown in a 100-mL volumetric flask turned in to the TA the previous week.
   - **You should provide a clean, labeled 100-mL volumetric flask to the TA for your unknown one week prior to this experiment.**

2. Obtain 100 mL of stock ferrous ammonium sulfate ($Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$) solution from the teaching assistant in a clean Erlenmeyer flask. Be certain to note the mass of ferrous ammonium sulfate used by the TA to make the solution and the final volume of the solution prepared by the TA.

3. Label five additional 100-mL volumetric flasks as Std. 1, Std. 5, Std. 10, Std. 25 and blank.

4. Into the standard volumetric flasks, pipette 1, 5, 10 and 25 mL aliquots of the standard iron solution.

5. To each of the 6 flasks, add 1 mL of ~1.4 M hydroxylamine hydrochloride, 10 mL of ~5 mM 1,10-phenanthroline, and 8 mL of ~1.2 M sodium acetate (a buffer). DO NOT PUT YOUR PIPETTES INTO THESE SOLUTIONS; pour a small amount into your beaker and pipette from this. **Be <u>sure</u> to add the reagents in the order shown here.**

6. Fill each flask to the mark with deionized water, mix well and allow to stand for 10 minutes.

7. Find a matching set of cuvettes; fill one cuvette with the analytical blank and fill the other with Std. 10.

8. Set the wavelength at 400 nm and zero the instrument.

9. Measure the absorbance of the standard in 20 nm increments in the range of 400 to 600 nm; you must re-zero the instrument every time you change the wavelength.

10. Determine the wavelength in this range which resulted in the maximum absorption. From this wavelength, measure the absorbance at +/- 15 nm in 5 nm increments. (a 30 nm range).

11. Set the wavelength to the wavelength where the maximum absorbance was observed and measure the absorbance of all standards and the unknown.

NOTE: All iron solutions should be discarded into a "Heavy Metal" waste container.

Notes:

1. For the calibration curve, select the x-y scatter chart that shows only the data points, then perform a best-fit line of your data without forcing the line through the origin.

2. To determine ppm iron, you need to know that ferrous ammonium sulfate is $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ and has a molecular weight of 392.14 g/mol. Note that ferrous ammonium sulfate is sometimes abbreviated as "FAS".

Outline of Calculations:

1. You need to determine the concentration of the calibration stock solution in ppm Fe (mg Fe/L). Start with the stated concentration in (g FAS / L). You can do the conversion in either of two equivalent ways:

a. Convert to (moles FAS / L), then to (moles Fe / L) then to (g Fe / L) then to (mg Fe/L) Use the fact that there is one Fe per formula unit of FAS. For other steps in this multi-step calculation you use the molar mass of FAS and the atomic mass of Fe.
b. Take (g FAS / L) and directly convert to (g Fe / L) by multiplying by the ratio of the atomic weight of Fe to the molar mass of FAS, since there is one Fe per formula weight of FAS. Then convert (g Fe / L) to (mg Fe / L)

2. Next you need to do dilution calculations for each individual iron standard solution, seeking to determine the concentration of the final solution (as tested in the spectrometer) in ppm Fe (mg Fe / L). The basic equation is conc1 x vol1 = conc2 x vol2.
    a. Conc1 would the concentration of the calibration stock solution in ppm Fe.
    b. Vol1 would be the volume of that stock solution you use. Be careful to express Vol1 and Vol2 in the same units (e.g. both in mL).
    c. Vol2 would be the final diluted volume of your diluted standard solution.
    d. Conc2 is the concentration of the diluted standard solution, in ppm Fe. Solve for this value!
3. Use the calculated concentrations of the diluted standards as the x values for graphing your calibration curve, paired with the absorbance values (as the y value) for those solutions.
4. Use the equation of your best fit line on the calibration curve to determine the concentration of iron (in ppm Fe) in your unknown sample. Use correct sig. figs. That value (the concentration of iron in the diluted solution, as measured in the spectrometer is the final value you are expected to report. You do not need to do further calculations.

Laboratory Report:

1. Name, date, and unknown number.
2. Full sample calculations, with good organization, correct units and correct sig. figs.
3. Concentration of the unknown, in ppm Fe.
4. Important chemical reactions.
5. Plot absorbance vs. wavelength (from steps 9-10) and indicate where λ_{max} occurs.
6. Plot absorbance vs. concentration. Be sure to include the zero concentration standard as one of your data points! Show the best fit line and its equation. Report the slope, intercept, and $\varepsilon_{\lambda max}$. Also report the uncertainties in slope and intercept (sm and sb). See Harris textbook, pp. 83-84. Using Excel to calculate sm and sb is recommended (use regression analysis).
7. Submit a one page discussion of your results. It should include among others, an analysis of the standard deviations, mean results, possible sources of error and how they can be corrected.
8. Answer the discussion questions

DISCUSION QUESTIONS:

1. Why do we use a “reagent blank” and not just distilled water to zero the spectrometer?
2. What would the effect be of waiting 30 minutes instead of 10 minutes on step 6?
3. Today’s unknown samples are simple iron dissolved in water. If our sample were more complex, it might contain other compounds, some which might be colored, including some which might absorb light at the same wavelength as the iron phenanthroline complex. What problem would this cause? How could we modify our procedure to correct for this problem?
4. State the function of each reagent in this experiment: 1,10-phenanthroline, hydroxylamine hydrochloride, sodium acetate.
5. The analytical sensitivity of the method depends on the slope of the calibration curve. Was your method sensitive for the determination of iron in these samples? Why?