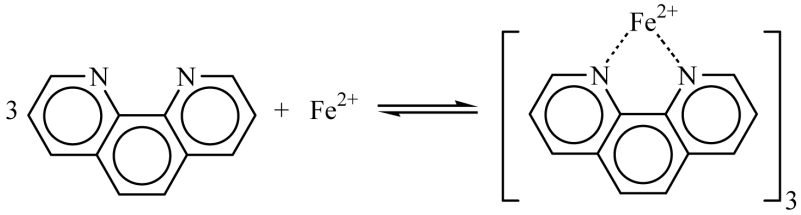
# CHEM 334 Quantitative Analysis Laboratory

## *Spectrophotometric Determination of Iron*

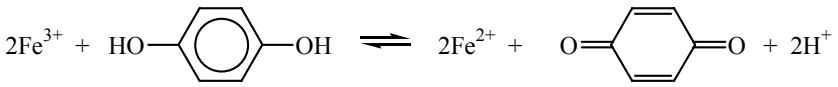
## Introduction

Aqueous iron, in its reduced ferrous form ($Fe^{2+}$), can be determined spectrophotometrically from its intensely colored complex with 1,10-phenanthroline (also *o*-phenanthroline, $C_{12}H_8N_2$, FW 180 g $mol^{-1}$), in acidic (pH 3-4) solution, by the following reaction (note the stoichiometry):




*o*-Phenanthroline $\lambda_{max}$ = 508 nm (1)

In our highly oxidizing environment, iron most often exists as the more oxidized ferric ion ($Fe^{3+}$) and must be reduced in order for the reaction in equation (1) to proceed. Hydroquinone ($C_6H_6O_2$, FW 110 g $mol^{-1}$) serves as a convenient reductant as seen in the following reaction:




Hydroquinone Quinone (2)

Citric acid, $C_3H_5O(COOH)_3$, is a weak, triprotic acid and its conjugate base, citrate, as its salt trisodium citrate, ($C_3H_5O(COONa)_3 \bullet 2H_2O$, FW 294 g $mol^{-1}$) serves to neutralize excess acid (*vide infra*) while the acid-conjugate base pair buffer the solution at the required pH value.

This method is well suited to the determination of iron in dietary supplements. It is necessary to release the iron ions from the mix of compounds that makes up the solid or liquid supplement. Digestion with moderately concentrated acid and at elevated temperature is an effective procedure for affecting this release.

## Procedures

**Preparation of Standard Iron Solution:** Prepare 100 mL of solution of approximately 1 mM but accurately known concentration ferrous ammonium sulfate ($Fe(NH_4)_2(SO_4)_2 \bullet 6H_2O$, FW 392 g $mol^{-1}$) in approximately 10 mM sulfuric acid. Use the solid salt and 1 M sulfuric acid to make up this solution in a volumetric flask. This solution can be stored in a polyethylene bottle or in glass.

**Other Reagents:** Obtain or prepare (only if you cannot obtain them) several solutions: 50 mL of a solution of 10 mM hydroquinone in water, 50 mL of a solution of 0.2 M sodium citrate in water and 50 mL of a solution of 20 mM phenanthroline in 10 % (v/v) ethanol in water (the solid is first dissolved in one-tenth volume ethanol then made up to the final volume with water). These solutions are prepared without volumetric glassware (why?) and can be stored in

polyethylene or in glass. Note the required accuracy of the concentrations of the solutes and recognize that the use of volumetric flasks is not required for the preparation of the solutions.

**Assay of Known Sample Solution:** Pipet a <=5.0 mL aliquot of the solution to be analyzed into a 50-mL volumetric flask. Add the required amount of sodium citrate solution to bring the pH of the solution is approximately 3.5 (see **Adjustment of the pH …**). Add 1.0 mL of hydroquinone solution and mix thoroughly. Add 1.0 mL of the phenanthroline solution and mix thoroughly. Fill to volume with water. Prepare a blank by preparing a solution with all reagents excepting the iron-containing solution. Measure the absorbance of the solution at 508 nm against the blank and using the same cuvette.

**Adjustment of the pH of an Assay Solution:** Pipet a 5.0 mL aliquot of the solution to be analyzed into a small beaker and add a few (three or four) drops of methyl yellow (0.1 g $L^{-1}$ in ethanol). Add sodium citrate solution drop-wise with swirling until the pH of the solution is approximately 3.5 as indicated by a peach color of the solution (the amount of citrate solution required will vary according to the amount of acid in the test solution). Discard this solution.

**Generation of a Calibration Curve:** Prepare five solutions using this procedure with 5.0, 4.0, 3.0, 2.0 and 1.0 mL aliquots of the standard iron solution. Use a volume of sodium citrate solution ***in proportion*** to the volume of iron solution used.

**Preparation of Unknown Sample Solution:** Accurately weigh one iron-containing supplement tablet. Digest the tablet in a 100-mL beaker in the hood using approximately 5 mL of 6 M hydrochloric acid on a hot plate set at 150°C for ten minutes. The tablet will not dissolve completely. Let the solution cool slightly (in the hood) and then quantitatively transfer (on the bench) all the contents of the beaker into a 100-mL volumetric flask. After cooling the solution completely to room temperature, fill to volume with water. There may be some sediment in the flask; let it settle for a few minutes. This is the **undiluted unknown stock** solution. Dilute this solution by pipetting 5.0-mL of the clear (not necessarily colorless) supernatant into a 100-mL volumetric flask and fill to volume with water. This is the **diluted unknown stock** solution. (What is the dilution factor used here?)

**Assay of Unknown Sample Solution:** Perform the iron assay described above in triplicate using three separate 5.0-mL aliquots of the diluted unknown stock solution. Note that it may require a greater or lesser amount of sodium citrate solution to neutralize the greater amount of acid in the unknown solution. Measure the absorbance of the three solutions against one freshly prepared blank solution as described previously.

**Analysis:** The molar absorptivity for the iron-phenanthroline complex at 508 nm is determined by fitting a linear function to the set of absorbance versus concentration measurements. The concentration of iron in the diluted unknown solution is found by the application of Beer's law and the molar absorptivity for the iron-phenanthroline complex. Calculate the mass of elemental iron in the original tablet based on the dilutions performed.

## Results

Report the molar absorptivity for iron-phenanthroline complex at 508 nm in units of $M^{-1}cm^{-1}$. Include a suitable uncertainty analysis for this value. Report the values of the determined mass of iron in the tablet as mass elemental iron. Include a suitable uncertainty analysis for this value.

## Discussion

Discuss your experimental results. Compare your measurement with the manufacturer's label information. Perform any and all conversions to make this comparison clear. Decide and report whether the tablet manufacturer should be hauled into criminal court for fraud or applauded for "truth in advertising." Justify your decision.

## References


- Atkins, R. C. *J. Chem. Educ.* **1975**, *52*, 550.