

Spectrophotometric Determination of Iron

Purpose

To become familiar with the principles of calorimetric analysis and to determine the iron content of an unknown sample.

Summary

Iron +II is reacted with o-phenanthroline to form a coloured complex ion. The intensity of the coloured species is measured using a Spectronic 301 spectrophotometer. A calibration curve (absorbance versus concentration) is constructed for iron +II and the concentration of the unknown iron sample is determined.

Theory

Colorimetric analysis is based on the change in the intensity of the colour of a solution with variations in concentration. Colorimetric methods represent the simplest form of absorption analysis. The human eye is used to compare the colour of the sample solution with a set of standards until a match is found.

An increase in sensitivity and accuracy results when a spectrophotometer is used to measure the colour intensity. Basically, it measures the fraction of an incident beam of light which is transmitted by a sample at a particular wavelength. You will use a Spectronic 21 in this experiment.

There are two ways to measure the difference in intensity of the light beam. One is the percent transmittance, %T, which is defined as:

$$\%T = \frac{I_o}{I} = \log \frac{1}{T} = -\log T$$

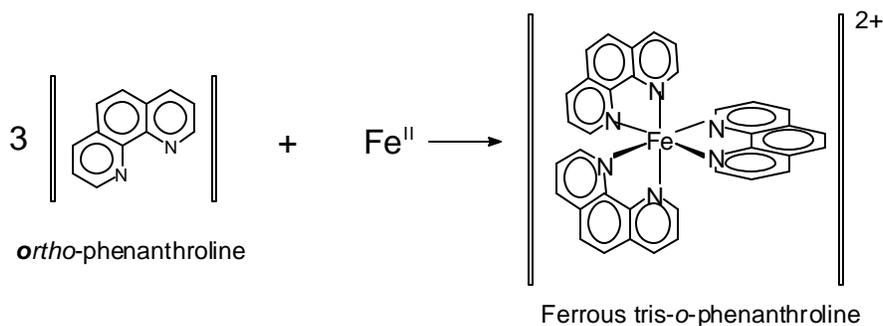
For any given compound, the amount of light absorbed depends upon (a) the concentration, (b) the path length, (c) the wavelength and (d) the solvent. Absorbance is related to the concentration according to the Beer-Lambert law:

$$A = \epsilon bc$$

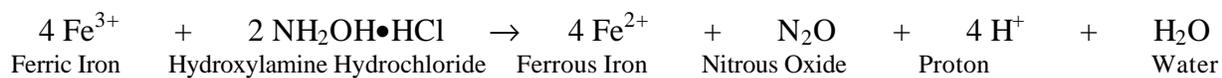
where ϵ is the extinction coefficient ($M^{-1}cm^{-1}$), b is the solution path length (cm) and c is the concentration (moles litre⁻¹).

Not all substances obey the linear Beer-Lambert law over all concentration ranges. Therefore you will construct a calibration curve that will provide the relationship between concentration and absorbance under the conditions used for the analysis.

In this experiment, you will analyze for iron by reacting iron +II with o-phenanthroline to form an orange-red complex ion according to the following equation:



Because we are starting with an Fe^{3+} solution and in order to be quantitative, all of the iron must be reduced from Fe^{3+} to Fe^{2+} by the use of an excess of hydroxylamine hydrochloride.



Safety

The wearing of safety glasses/goggles is mandatory at all times. Those students wearing prescription glasses must wear goggles over their glasses. Students without prescription lenses must wear the safety glasses provided. Contact lenses should not be worn in the lab. Safety glasses/goggles

Procedure: (note - work in pairs)

1. The STANADRD IRON solution contains 0.2500 g/L of pure iron. Pipet 25.00 mL of this standard iron solution into a 500 mL volumetric flask and dilute up to the mark with distilled water.
2. Prepare the following iron calibration solutions by pipetting the indicated amounts of the above iron solution (step 1) into labeled 50 mL volumetric flasks. The first flask is a blank containing no iron.

Concentration of Fe	Volume to pipet
0.00 mg Fe	0.00 mL
0.05 mg Fe	4.00 mL
0.10 mg Fe	8.00 mL
0.15 mg Fe	12.00 mL
0.20 mg Fe	16.00 mL
0.25 mg Fe	20.00 mL

3. Pipet 10.00 mL of an unknown sample solution (record the unknown's number) into a 250 mL volumetric flask and dilute to the mark with distilled water. Invert and shake the flask several times to mix the solution.
4. Pipet two 25.00 mL aliquots of this solution into two 50 mL volumetric flasks labeled unknown.
5. Using a 10 mL graduated cylinder, add 4.0 mL of 10% hydroxylamine hydrochloride solution and 4.0 mL of 0.3% o-phenanthroline solution to each volumetric flask.
6. Swirl and allow the mixture to stand for 10 minutes.
7. Dilute each flask to the mark with distilled water and mix well by inverting and shaking the capped volumetric flasks several times.
8. Using the Spectronic 301 spectrophotometer, carefully measure the percent transmittance of the various solutions in the 50 mL volumetric flasks, including the two unknown solutions. Record your results in the following table.

Solution	% Transmittance	Absorbance ($A = -\log T$)
0.00 mg Fe (blank)	100%	0
0.05 mg Fe		
0.10 mg Fe		
0.15 mg Fe		
0.20 mg Fe		
0.25 mg Fe		
Unknown 1		
Unknown 2		

Calculations and Discussion

1. Prepare a plot of absorbance versus concentration of the known solutions (express the concentration in mg Fe per 50 mL of solution). Draw the best fitting straight line through the points – this is called the **Beer-Lambert Law** plot.
2. Place the best Absorbance value of each unknown solution onto this plot and determine their concentrations.
3. Calculate the amount of iron in the unknown sample. Express this as mg of Fe per litre of the original unknown solution (mg/L Fe).

E.g. From the graph you obtain a concentration of 0.10 mg Fe/50 mL

Since in step 3 we diluted the original sample 25 times and in step 4, 2 more times the concentration of the original sample is therefore:

$$0.10 \frac{\text{mg Fe}}{50\text{mL}} \times 50 (\text{dilution factor}) \times \frac{1000\text{ mL}}{\text{L}} = \frac{100\text{ mg Fe}}{\text{L}}$$

4. Compare your results with the accepted value

Unknown #1	Unknown #2	Unknown #3	Unknown #4
173.5 mg/L	209.2 mg/L	225.6 mg/L	242.7 mg/L

and calculate the **relative error**.

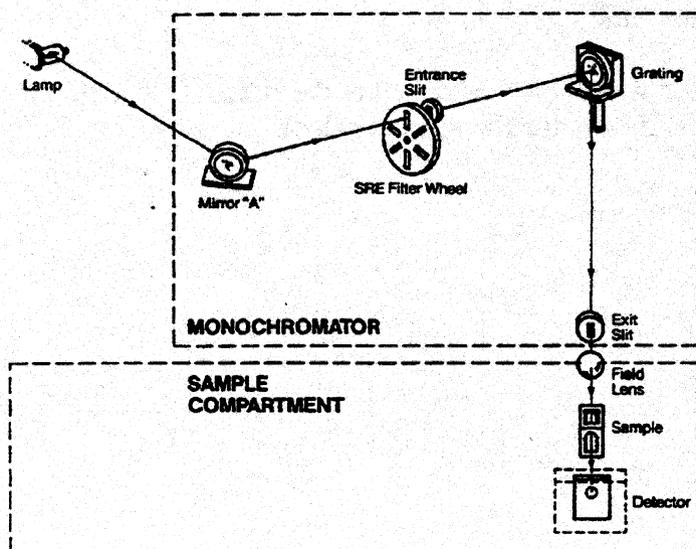
$$\text{relative error} = \frac{\text{experimental value} - \text{accepted value}}{\text{accepted value}} \times 100\%$$

References

1. Skoog and West, Fundamentals of Analytical Chemistry, 2nd Ed., Chapter 29.
2. Vogel, A Textbook of Quantitative Inorganic Analysis, 3rd Ed., p. 294, 310 and 787.

APPENDIX D

The Spectronic 20/21/301 Spectrophotometer



Basically a spectrophotometer is an instrument which measures the fraction (I/I_0) of an incident beam of light (I_0) which is transmitted (I) by a sample of a particular wavelength. The instrument consists of five fundamental components:

1. A light source (tungsten) which emits light with a wavelength range ~350 to 1000nm.
2. A monochromator which selects a particular wavelength of light and sends it to the sample cell with an intensity of I_0 .
3. The sample cell to hold the solution being analyzed.
4. A detector which measures the intensity of the transmitted light (I) from the sample cell. (note $I < I_0$).
5. A meter which indicates the intensity of the transmitted light.

The amount of light absorbed by any given substance depends upon (a) the concentration (b) the cell or path length (c) the wavelength of light and (d) the solvent. There are two ways to express the amount of light absorbed. One is percent transmittance defined as:

$$\%T = \frac{I}{I_0} \times 100\%$$

The other method is in terms of absorbance (optical density, O.D) which is defined by:

$$A = \log \frac{I_0}{I}$$

Absorbance is related to the concentration by the Beer-Lambert law:

$$A = \epsilon bc$$

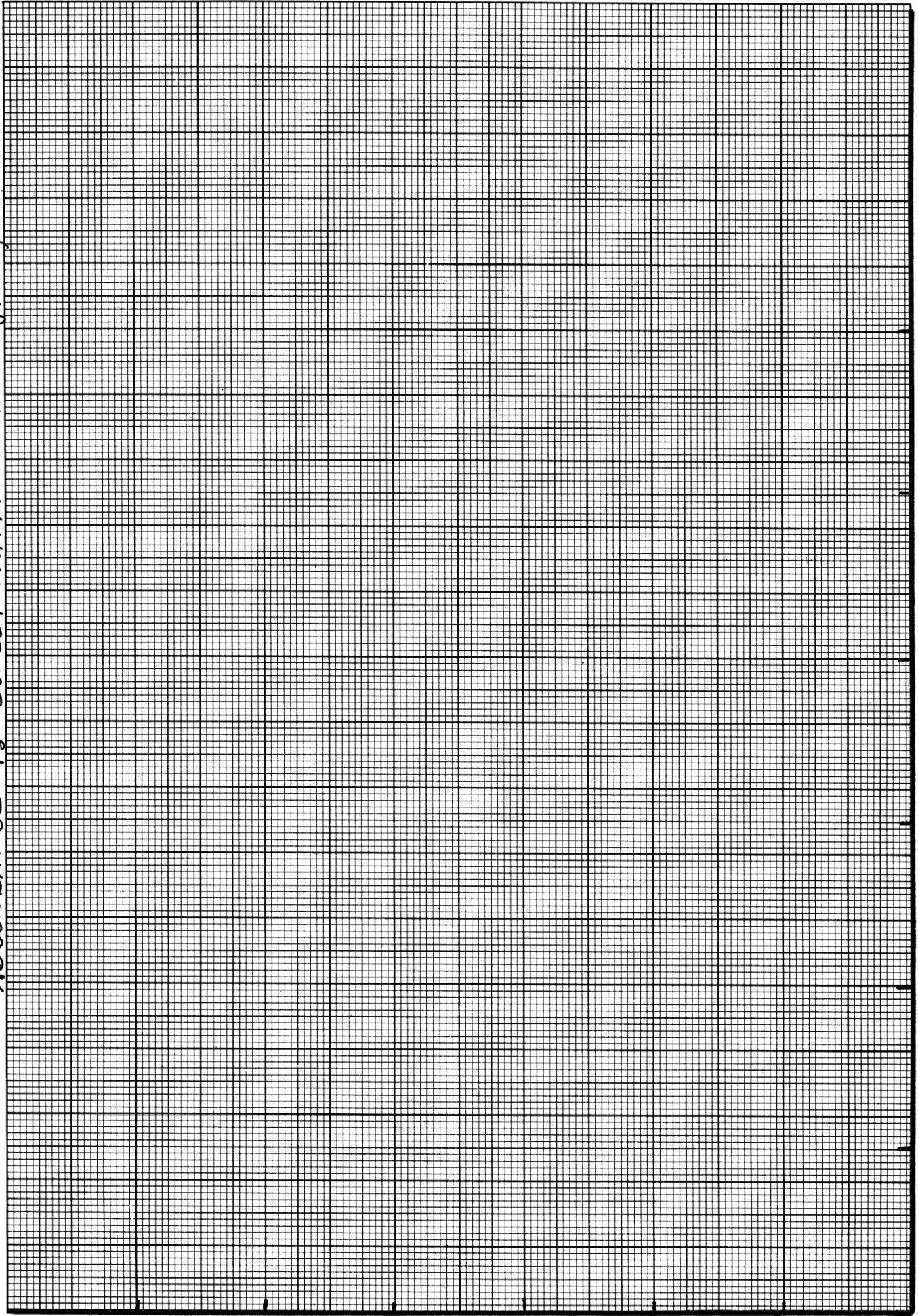
where A = absorbance

ϵ = extinction coefficient ($M^{-1}cm^{-1}$)

b = solution path length (cm)

c = concentration ($mol L^{-1}$)

ABSORBANCE vs CONCENTRATION Fe (mg/ml)



1.2

1.0

0.0

0.2

0.4

0.6

0.05

0.10

0.15

0.20

0.25

0.30

ABSORBANCE

Iron Concentration (mg/ml)