Experiment 3

SPECTROPHOTOMETRIC DETERMINATION OF DISSOLVED IRON

REFERENCE: Text, Chapter 18, Sect. 18-1 → 18-4; (also see similar lab at www.whfreeman.com/qca experiment 19).

INTRODUCTION

Iron can exist in natural waters where it originates from the dissolution of minerals. Even though most iron containing minerals are not very soluble in water (as can be seen from the solubility products for the iron oxides and iron-containing salts), a finite amount of iron still dissolves and is usually found in the form of Fe^{3+} ion. Another source of iron in water in your home can originate from so-called galvanized pipes. If you have ever lived in an older home, there is a high probability that the water pipes are made out of iron. These pipes tend to rust (i.e. elemental iron oxidizes to form iron-oxides), and you can readily observe the iron oxide as a reddish color in the water coming from the tap. Since these iron pipes corrode the iron oxides deposit on the pipe walls causing the internal diameter of the galvanized pipes to become quite small. This, in turn, results in a reduction of water pressure.

While the latter is a minor inconvenience, the presence of lead (in the form of Pb^{2+}) in water can cause major health problems, particularly for children younger than 4. Ingestion of high levels of lead results in permanent mental impairment of young children. The lead primarily originates from lead-containing solder that has been used in the past. While spectrophotometry allows us to analyze for lead in water, in this lab, we'll be analyzing for the presence of slightly more benign metal such as iron. You'll notice that we are analyzing for very low levels of iron in your water unknown, a few parts per million; 1 ppm = 1 mg/L. These levels are indicative of the levels which you are likely to encounter in the environment. It should be noted, however, that nowadays water pipes are made from copper pieces that are soldered together with lead-free solder.

In this procedure, iron in its naturally occurring form is first converted to a colored compound, one that is needed because it readily absorbs light. In this procedure, Fe^{3+} ions from the water sample first need to be reduced to Fe^{2+} using hydroquinone as a reducing agent.

Fe^{2+} ions readily form metal complexes with 1,10-phenanthroline that are red-orange colored. The reagent is a weak base that reacts to form phenanthrolinium ion, $PhenH^+$, in acidic media. The complex can be described by the following equation:

$$Fe^{2+}(aq) + 3\ PhenH^+(aq) \rightarrow Fe(Phen)_3^{2+}(aq) + 3\ H^+(aq)$$

The equilibrium constant for this reaction is 2.5×10^6 at 25 °C. Fe^{2+} ions form this complex ($Fe(Phen)_3^{2+}$) in the pH range between pH = 3 and pH = 9. A pH of about 3.5 is ordinarily recommended to prevent precipitation of iron salts. The complex, once formed, is very stable.

SAMPLE

Obtain approximately 100 mL of an unknown aqueous sample from your instructor.

PROCEDURE

Preparation of solutions

Calculate the volumes of stock solution that are needed in order to prepare a series of 4 standard solutions whose concentrations will span in the range from 0-4 ppm. Assume that the concentration of Fe^{2+} in the stock solution is ~10 ppm.

From the Fe^{2+} stock solution provided, prepare standard solutions of Fe^{2+} in 100.00 mL volumetric flasks. The Fe^{2+} concentration should span the range from 1 to 4 ppm Fe^{2+}. Using a volumetric pipette(s) transfer the required amount(s) of stock solution (ones that you had pre-calculated) into the volumetric flask(s). *Note: Only volumetric pipettes have the required accuracy for preparation of standards*. The exact concentration of the stock solution is written on the reagent bottle – make sure that you write down this concentration in your notebook. In order to obtain the exact concentrations of your standard solutions you will use this value (NOT just the approximate concentration of 10 ppm).

For the blank solution, start by adding ~30 mL of deionized water to a 100.00-mL volumetric flask.

For the unknown solution, start by pipetting 25.00 mL of your unknown into a 250.00-mL volumetric flask.

Add ~1.0 mL of the hydroquinone solution to each of the flasks (standards, blank, and unknown) *(to reduce Fe^{3+} to Fe^{2+})* and ~5.0 mL of the 1,10-phenanthroline solution *(to form the colored complex which can be analyzed spectrophotometrically)*. Then add ~8.0 mL of acetic acid/sodium acetate buffer solution in order to produce the red color of ferrous 1,10-phenanthroline. *(The buffer fixes the pH to around 4, a value at which the complex forms.)* Dilute each solution to exactly 100.00 mL (except your unknown which you'll need to dilute to 250.00-mL). Be sure that all reagents have been added to the volumetric flasks before you fill the flasks with deionized water to the mark. Allow at least 15 min after adding the reagents for the color of the complex to develop; i.e., give time for the reaction to go to completion. Once developed, the color is stable for hours.

For your blank, standards, and unknown, find the absorbance using the diode array spectrometer as described below. These data will be used in your calculations to determine the concentration of Fe^{3+} in your unknown.

Data Acquisition

Use the diode array spectrophotometer. An excellent resource on how to use this instrument is at the following web address, which you should consult:
http://www.eiu.edu/%7Eeiuchem/GenChem/EquipmentGuide/diodearray.pdf

Here is an abbreviated version of how to use this spectrometer.

1. Obtain a rectangular cuvet. Two sides of the cuvet are frosted and two are transparent. There is an alignment arrow at the top of one of the transparent sides. Handle the cuvet by the frosted sides only. Always wipe the transparent sides with a Kimwipe prior to inserting the cuvette into the sample compartment.

2. Fill the cuvet two-thirds full with deionized water. Insert the cuvet into the sample compartment and orient it so that the arrow on the cuvet window and the white line on the sample compartment are aligned. Press firmly to insure the cuvette is firmly seated – the top half inch will protrude from the top of the sample compartment.

3. Acquire and store a reference spectrum by pressing the illuminated light bulb button.

4. Remove the cuvet from the sample compartment, discard the water, and shake out the excess onto a Kimwipe. Rinse the cuvet with a small portion of the solution of interest – your most concentrated standard initially. The entire visible spectrum is displayed. From this absorption spectrum, select an appropriate wavelength to use for quantitative analysis. Use this wavelength in all of your subsequent analyses, by setting the cursor to this wavelength.

5. Rinse the cuvet many times with distilled water to quantitatively remove the standard. It is important that no standard remain in the cuvet since this would alter all of your future measurements.

6. Rinse the cuvet with a small portion of your blank solution and discard the rinse. Fill the cuvet two-thirds full with a fresh portion of this solution. Wipe it with a Kimwipe and insert it into the sample compartment with the marks aligned. Obtain and record an absorbance reading.

7. Discard the solution and shake out the excess onto a Kimwipe. Rinse the cuvette with the next solution of interest (your most dilute standard) and discard. Fill the cuvette two-thirds full with this solution, wipe the outside with a Kimwipe and obtain an absorbance reading at the wavelength previously selected. Repeat with each of the standards in the order of increasing concentration, and lastly obtain an absorbance reading of the unknown.

Take all of your measurements in one session to minimize error from instrumental drift and/or other wavelength settings used by other students.

For next week: weigh approximately 4 g of potassium-hydrogen-phthalate (KHP) primary standard in a weighing bottle and place it in the oven at 110 °C to dry for about 2 h. Pick an unknown sample, pour the contents into a weighing bottle and dry it in the oven at 110 °C for about 2 h. (Because KHP thermally decomposes over time, you should not leave it in the oven until next week.)

CALCULATIONS – Concepts

Using the absorbance data for the blank and the standard Fe^{2+} solutions, make a plot of absorbance (y-axis) versus Fe^{2+} concentration (x-axis), in a similar way that you had done in Experiment 2. This may be termed a "Beer's Law Plot", since Beer's Law states that there should be a linear relationship between absorbance and analyte concentration ($A = \epsilon bc$). Using this plot and data, perform a linear regression on the data to find the best straight line fit to the data. The equation for this straight line can then be used to find the concentration of the unknown solution, since an absorbance value for it has been experimentally obtained.

Remember that the iron concentration you calculate is for the unknown sample that was analyzed. The value that should be reported is for the unknown sample as it was provided to you. Thus any dilutions in preparing the sample for analysis must be taken into account. Finally, the iron concentration reported has uncertainty associated with it which should be computed in a way similar to the one performed the previous week.

Fill out and hand in the results sheet on the following page.

Spectrophotometric Analysis Results Sheet

Name: _____

Unknown Number: _____

Standards

Fe^{3+} Concentration (ppm)	Absorbance
0 (blank)	

Slope ± standard deviation (error) of calibration line:_____
y-intercept ± standard deviation (error) of calibration line: _____
standard deviation (error) of absorbance of calibration line: _____

Unknown Absorbance: _____

Fe concentration (ppm) of unknown solution as analyzed ± standard deviation: _____

Fe concentration (ppm) of original unknown solution ± standard deviation: _____
(This is your reported result.)

Fe solution concentration (to be filled in by grader): _____

95% Confidence Interval ppm Fe^{2+}: _____

Grade _____