Water Quality 1 - Spectrophotometric Determination of Iron in Drinking Water

Introduction

The safety of drinking water is a very important public health issue. The United States and World Health Organization have established well-defined standards for drinking water purity. For example, U.S. Federal regulations limit the amount of iron to less than 0.3 ppm (0.3 mg/L) in municipal drinking water. Although iron is only toxic at very high concentrations, it acts as a useful surrogate for other heavy metals, whose presence in drinking water is a real danger to public health. In this experiment we will determine the levels of iron present in the tap water you drink (both cold and hot) to determine whether or not the water meets the standards. Try to remember to bring bottles of tap water to the lab, since this will be more interesting if it's YOUR water that you're testing. You will also determine the iron in two "unknown" challenge samples that you will prepare in the lab.

A commonly used method for the determination of trace amounts of iron involves the complexation of Fe^{2+} with 1,10-phenanthroline (phen) to produce an intensely red-orange colored complex:

$$Fe^{2+} + 3\ phen \rightarrow Fe(phen)_3^{2+}$$

Since the iron present in the water predominantly exists as Fe^{3+}, it is necessary to first reduce Fe^{3+} to Fe^{2+}. This is accomplished by the addition of the reducing agent hydroxylamine. An excess of reducing agent is needed to maintain iron in the +2 state (because dissolved oxygen will reoxidize Fe^{2+} to Fe^{3+}). Fe^{2+} is quantitatively complexed by 1,10-phenanthroline in the pH range from 3 to 9. Sodium acetate is used as a buffer to maintain a constant pH at 3.5. If the pH is too high, the Fe^{2+} will be oxidized to Fe^{3+}; if the pH is too low, H^+ will compete with Fe^{2+} for the basic 1,10-phenanthroline (to form $phenH^+$). Either way, you won't get complete complexation. You should discuss these possible problems and their impact in the Introduction section of your report. The determination of the iron-phen complex is performed with a spectrophotometer at a fixed wavelength of 508 nm using external calibration based on iron standard solutions.

Apparatus

plastic cuvette (1)

500 mL volumetric flask (1)

50 mL volumetric flasks (10)

500 µL automatic pipettor (1)

1 mL pipet (1)

5 mL pipets (2)

25 mL pipet (1)

Instrumentation (See Appendices for Operating Instructions)

WPA Biowave II or other benchtop UV-Vis spectrophotometer

Solutions available

(1) 0.29 M hydroxylamine hydrochloride (NH_2OH•HCl): measure out about 12 mL to a small beaker.

(2) 5.0 $x10^{-3}$ M 1,10-phenanthroline: measure out about 50 mL to a 100 or 200 mL beaker.

(3) 1.2 M sodium acetate: measure out about 50 mL to a 100 or 200 mL beaker.

(4) 2 M H_2SO_4 (Caution: strong oxidizing acid.)

Solution to be prepared

Standard iron solution (5.0 $x10^{-4}$ M). Accurately weigh out about 0.100 g $Fe(NH_4)_2(SO_4)_2$-$6H_20$ (FW = 392.14). Transfer quantitatively into a 500-mL volumetric flask. Add about 10 mL of 2 M H_2SO_4 and 50-mL deionized water to the flask to dissolve the $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ completely. Fill the flask to the mark with deionized water and mix thoroughly.

Procedure

(1) Preparing the working standard solutions

Use the 500 µL automatic pipettor to pipet 0, 0.5, 1.0, 1.5, 2.0, and 2.5 mL of the standard iron solution into a series of six 50 mL volumetric flasks. Pipet the following solutions into each of the six volumetric flasks.

a) 1 mL of the hydroxylamine solution
b) 5 mL of the sodium acetate solution
c) 5 mL of the 1,10-phenanthroline solution

Fill each flask to the mark with deionized water and mix thoroughly. Allow the solutions to stand for 10 min. Mix the solutions again before measuring the absorbance. *If more than half of the standard iron solution remains when you complete the experiment, you can retain it for the other experiment in this set.*

(2) Measuring the blank

To determine any possible absorbance from the matrix (*i.e.*, the other reagents), deionized water will be used as the blank. Rinse the cuvette several times with tap water followed by deionized water, fill it with deionized water, place it the holder, and blank the spectrometer.

(3) Measuring the standards

Rinse the cuvette with each solution (including the zero iron concentration sample) three times, and then fill it with the solution, place it in the holder, and measure the absorbance. Repeat the measurement with a fresh aliquot of the solution (no need to rinse this time.) The two absorbance values should be similar, otherwise you should measure another one. If you work from lowest iron concentration to highest, you will minimize the potential for carryover.

(4) Measuring the unkown water samples

Prepare two challenge “unkown” samples, one that will end up near mid-range on the calibration curve and one near the lower end, to test for method recovery and accuracy. Pipet 25 mL aliquots of your cold and hot tap water and two unknown samples into four 50 mL volumetric flasks. Finish preparing the samples as described in the procedure (1). Measure the absorbance of the solutions. If the absorbance is outside of the range of the iron standards, you should repeat the measurement after adjusting the concentration to bring it into the range of the standards. If it is too concentrated, you can simply use a smaller volume of the sample. If it is too dilute, you may try evaporative concentration, if time permits. Be sure to document any deviations from the suggested procedure in the Experimental section of your report.

Report: In preparing the Partial Report for this part of the experiment, you should consider/complete/discuss the following:

(1) Calculate the analytical concentration of iron in the standard iron solutions. Tabulate the observed absorbance and the derived concentrations (in ppm and molarity) of iron for all the standards, tap water samples, and unknown samples. (Do not forget to consider the dilution factors in your calculations.) Comment on the recovery and accuracy of the determination, based on the challenge unknowns. Calculate the limits of detection and quantitation of the method based on the standard error of the intercept. If any of your unknowns are below these limits, how should their concentration be reported?

(2) Plot the absorbance vs. iron concentration for the standards (including the iron-free solution.) Use the method of least-squares (*i.e.*, linear regression) to derive the Beers law equation in the form of A = m[Fe]+b. Be sure to report the calibration equation in the Results and Abstract sections of your report. If the intercept has a non-zero value, explain why, and comment on the R^2 value.

(3) Calculate the molar absorptivity of $Fe(phen)_3^{2+}$ at 508 nm. Compare your value with the literature value, 11,100 $M^{-1}cm^{-1}$. Explain possible causes for the difference, if any is observed.

(4) Comment on whether or not the water samples meet the Federal standards for drinking water and any differences observed between the cold and hot water from the same tap.

Revised 1/6/2012 - DBA