Experiment 7: Adsorption Spectroscopy I, Determination of Iron with 1,10-Phenanthroline

Procedure

In this experiment, we aim to determine the Na concentration of an unknown sample by measuring an emission intensity of unknowns and comparing the measurements to a calibration curve created from solutions of known concentrations.

First, turn in a 100mL volumetric flask to TA for unknown at least one day before doing the experiment. Weigh out about 0.07g of ferrous ammonium sulfate, dissolve in water, and transfer to a 1000mL volumetric flask. Add 2.5mL of concentrated sulfuric acid and dilute to the mark. Now, prepare the standards. Using a pipet place 1, 5, 10, 20, and 35ml of standard iron solution into five 100mL volumetric flasks. Also, place 50mL of H₂O in a sixth flask (for blank). Treat all samples (including unknown) in the following manner: pipet 1mL of hydroxylamine solution, 10mL of 1,10-phenanthroline solution and 8mL of sodium acetate solution into each flask and dilute to the mark. Mix and allow to stand for 10 min. Now, on the Spec 20 set the %T to zero with no cuvette in the compartment, using the disk on the left front. Set the %T to 100 using the right front dial, with the blank in the compartment. Recheck these settings frequently. Set the wavelength at 505nm (instructed to do so by Shawn) and record the %T within 0.2% for each of the standards and the usual unknown. Calculate the absorbance using $A=-\log(\%T/100)$ and the concentration for the standard. Plot a graph of absorbance vs. concentration of the standards using Tablecurve or Excel.

For detailed procedure refer to: Handout, Experiment 7, Absorption Spectroscopy I: Determination of Iron with 1,10-phenanthroline.

For further information on adsorption spectroscopy refer to:

Theory
In preparing the standards and the unknown the reaction of the ferrous iron with 1,10-phenanthroline yielded a red complex that served as a good sensitive method for determining iron:

$$\text{Fe}^{2+} + 3\text{C}_{12}\text{H}_{8}\text{N}_2 = [\text{Fe}((\text{C}_{12}\text{H}_{8}\text{N}_2)_3)]^{2+}$$

The molar absorptivity of this complex is 11,100 at 508nm. Prior to the development of the red-orange color, hydroxylamine is added as a reducing agent to put the iron the ferrous state:

$$2\text{Fe}^{2+} + 2\text{NH}_2\text{OH} + 2\text{OH}^- \rightarrow 2\text{Fe}^{2+} + \text{N}_2 + 4\text{H}_2\text{O}$$

The sodium acetate is added to adjust the pH to between 6 and 9. The color intensity remains relatively constant between pH 2 and 9.

During the analysis of the samples, the spec 20 is calibrated by using the blank sample which contained all species except the iron solution. By doing this, we hoped to minimize the effects caused by reflection, absorption, etc. due to the presence of the other elements (ie, the cuvette and solvent). Failure to use a blank would have caused inaccurate % transmittance readings. Now, by placing the subsequent standards in the spec 20, the decreased %T was due only to the presence of the iron solution. In passing through the cuvette the power of the light beam is decreased as a result of the interactions between the photons and absorbing particles (the iron solution). The %T reading on the spec 20 results from the following ratio:

$$\%\text{T} = \frac{P}{P_0} \times 100\%$$

Where p is the power of the beam prior to entering the cuvette and $P_0$ is the power after passing through. The absorbance was calculated from the %T using the equation:

$$A = -\log\left(\frac{\%\text{T}}{100}\right)$$

It was not read from the scale on the Spec 20. Beer’s law states that “absorbance is linearly related to the generation of the absorbing species, c, and the path length, b, of the radiation in the absorbing medium.” (Skoog, 405). In my graph of absorbance vs. concentration, I used Tablecurve. In asking it to draw a curve that best fit my data points, it produced an exponential curve as its first choice, which obviously is not a linear graph. I went and showed the graph to Dr. Holler (After Shawn told me to get some assistance in making it a linear curve). He, at first, started to help me redo the graph. Then, he thought since the exponential graph was in fact the best fit, he said solve for c and use it. So, technically my graph is not linear, which would suggest it did not obey Beer’s Law. However the curve to the exponential is very slight, so essentially Beer’s Law was obeyed.

Structure of 1,10-phenanthroline
Data

Amount of ferrous ammonium sulfate: 0.0724g

%Transmittance at $\lambda=505\text{nm}$

<table>
<thead>
<tr>
<th>Conc (ppm)</th>
<th>%T</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.103</td>
<td>92.8%</td>
</tr>
<tr>
<td>0.515</td>
<td>76.6%</td>
</tr>
<tr>
<td>1.03</td>
<td>57.1%</td>
</tr>
<tr>
<td>2.06</td>
<td>32.3%</td>
</tr>
<tr>
<td>3.61</td>
<td>15.1%</td>
</tr>
<tr>
<td>Unknown</td>
<td>34.0%</td>
</tr>
</tbody>
</table>

Absorbance at 505nm

<table>
<thead>
<tr>
<th>Conc (ppm)</th>
<th>Abs</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.103</td>
<td>0.0324</td>
</tr>
<tr>
<td>0.515</td>
<td>0.116</td>
</tr>
<tr>
<td>1.03</td>
<td>0.243</td>
</tr>
<tr>
<td>2.06</td>
<td>0.491</td>
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<tr>
<td>3.61</td>
<td>0.821</td>
</tr>
<tr>
<td>Unknown</td>
<td>0.468</td>
</tr>
</tbody>
</table>

Calibration Curve
Calculations

Concentration of ferrous ammonium sulfate solution (FAS)

\[
\left( \frac{0.0714 \text{g FAS}}{1 \text{L}} \right) \times \left( \frac{1 \text{mol FAS}}{392.14 \text{g FAS}} \right) \times \left( \frac{55.84 \text{g Fe}}{1 \text{mol Fe}} \right) \times \left( \frac{1000 \text{mg}}{1 \text{L}} \right) = 10.3 \text{mg L} = 10.3 \text{ppm Fe}
\]

Calculation of absorbance:

\[
A = -\log \left( \frac{961}{100} \right)
\]

\[
A = -\log \left( \frac{12.010}{100} \right) = 0.0324
\]

Concentration of diluted standards:

\[
C_{\text{ml}} = \left( \frac{10.3 \text{mg Fe}}{L} \right) \times \left( \frac{1 \text{mL of Fe soin}}{100 \text{mL of total soin}} \right) = 0.103 \text{ppm}
\]

Concentration of unknown, determined from graph:
\[ y = a + be^{-\frac{x}{c}} \]
\[ y - a = be^{-\frac{x}{c}} \]
\[ \frac{y - a}{b} = e^{-\frac{x}{c}} \]
\[ \ln\left(\frac{y - a}{b}\right) = \frac{y - a}{b} \]
\[ \frac{y - a}{b} = \ln\left(\frac{y - a}{b}\right) \]
\[ x = \ln\left(\frac{y - a}{b}\right) \]
\[ x = -22.97311\ln\left(\frac{0.46682 - 6.34378269}{-6.34378269}\right) \]
\[ x = 1.99 \frac{mgFe}{L} = 1.99 ppm Fe \]

Molarity of unknown:
\[ \left(1.99 \frac{mgFe}{L}\right) \times \left(\frac{1g}{1000mg}\right) \times \left(\frac{1 molFe}{55.84gFe}\right) = 3.56 \times 10^{-5} M \]

**Results and Error Analysis**

Mean absorbance of unknown: 0.468

\( C_{Fe^{2+}} \) of unknown: 3.56x10\(^{-5}\)M

Parts per million: 1.99 ppm

I have no numerical error analysis for this experiment. Error sources will be discussed in discussion.

**Discussion**

In this experiment I determined the iron concentration in my unknown solution. I found that the concentration for my unknown was 3.56x10\(^{-5}\)M which is equivalent to 1.00 ppm. This value was determined by obtaining data from solutions of known concentration. These solutions were placed in the spec 20 and a %Transmittance reading was produced. The %T was used to determine the absorbance for the standards and the unknown. Then by plotting a graph of absorbance vs. concentration, an equation was produced from which the unknown concentration was determined (the eq. was solved for x concentration, which was the only unknown quantity in the equation). Error may have resulted from the fact that two different cuvettes were used. One was used for the blank solution (because it was used for frequent readings) and the other for the various standards and the unknown. Although the two cuvettes are very similar in all their characteristics, they are not exactly alike. Therefore, the amount of light reflected, scattered, and absorbed, etc. is different and thus, the %T is somewhat affected. In short, setting the 100%T with the cuvette containing the blank solution might have been different that if the cuvette used for the samples was also used for the blank solution.
Additional error may have resulted from pipetting slightly different amounts of each reagent into the different flasks. Naturally, there will always be some type of deviation when pipetting the same quantity into each flask. This deviation may have caused an increased or decreased amount of absorbance by solution components not of interest. For example, if the contents of the blank solution were slightly different than the 1mL standard the %T would be slightly affected because of the increased or decreased presence of other components. This error can be minimized by simply being careful in your pipetting techniques. The first error mentioned could be minimized by using only one cuvette for all samples, including the blank.