Lab 3: Concentration Determination of an Aqueous Solution

Laboratory Goals
• Compare different methods of concentration determination
• Use titration as a quantitative analysis technique
• Use spectrophotometry as a quantitative analysis technique

Safety Notes
1. A heated evaporation dish may take up to 15 minutes to cool to room temperature. Serious burns can result from evaporating dishes that may appear to be cool. To be safe, always use crucible tongs to handle evaporating dishes.
2. Both the concentrated ammonia and sulfuric acid solutions can cause serious burns. Be sure to avoid spilling any and immediately notify the LA and clean up any spills (put sodium bicarbonate on the spill to neutralize it).

Introduction
Often there is more than one method that can be used to obtain a solution to a particular problem. It is important to recognize the strengths and weaknesses of various methods since the accuracy and precision of your results depends on the method you choose.

The problem posed in this experiment is to find the concentration of a manganese (II) sulfate solution. You will use three methods to accomplish this task. The first is an evaporation method which removes the water from the solution. The second is a titration of the Mn$^{2+}$ ion in the solution, and the third is a spectrophotometric method. The results obtained from the three methods will be compared.

Evaporation method
The solution used contains some amount of manganese (II) sulfate monohydrate, MnSO$_4$·H$_2$O (also called manganous sulfate) dissolved in water. When a sample of this solution is evaporated to dryness and the solvent and the waters of hydration are driven off, solid MnSO$_4$ will remain.

The reaction sequence is as follows. As most of the water is evaporated, the manganese and sulfate ions initially coming together to form a salt, followed by evaporation of the residual water.

\[
\text{Mn}^{2+} (\text{aq}) + \text{SO}_4^{2-} (\text{aq}) + n\text{H}_2\text{O} (\text{aq}) \xrightarrow{\Delta 100 \^\circ C} \text{MnSO}_4 \cdot n\text{H}_2\text{O} (s) \\
\text{MnSO}_4 \cdot n\text{H}_2\text{O} \xrightarrow{\Delta 400-500 \^\circ C} \text{MnSO}_4 (s) + n\text{H}_2\text{O} (g)
\]
By knowing the volume of sample used and the weight of solid remaining, the concentration of the solution can be calculated.

Since we know that:

\[
FW \text{ MnSO}_4 = \frac{g \text{ MnSO}_4}{\text{mol MnSO}_4} \quad \text{or} \quad \text{mol MnSO}_4 = \frac{g \text{ MnSO}_4}{FW \text{ MnSO}_4}
\]

and

\[
M \text{ MnSO}_4 = \frac{\text{mol MnSO}_4}{L \text{ solution}}
\]

We should be able to determine the original molarity of the solution from the original volume of solution and the weight of salt remaining after heating.

**Titration of EDTA**

The manganese (II) sulfate solution contains the Mn\(^{2+}\) ion. EDTA, the abbreviation for ethylenediaminetetraacetate, is one of a class of compounds known as chelating agents. The disodium EDTA used in this experiment reacts with Mn\(^{2+}\) in a 1:1 ratio.

By titrating a known amount of EDTA with the manganese (II) sulfate solution its concentration can be determined. At the equivalence point of the titration the moles of Mn\(^{2+}\) equals the moles of EDTA added.

\[
\text{H}_2\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8^{-2} (aq) + \text{Mn}^{2+} (aq) \rightarrow \text{MnC}_{10}\text{H}_{12}\text{N}_2\text{O}_8^{-2} (aq) + 2\text{H}^+ (aq)
\]

Moles EDTA = moles Mn\(^{2+}\) and

Molarity of solution = moles Mn\(^{2+}\) / volume Mn\(^{2+}\)

**Spectrophotometric Determination**

Manganese is a transition metal, many of which form colored compounds. In this experiment, the Mn\(^{2+}\) ion is converted to the permanganate ion, MnO\(_4\)\(^{2-}\), which absorbs visible light and is dark purple in color. The conversion is done by reacting the manganese ion with persulfate ion, using silver ion as a catalyst. The reaction is as follows.

\[
2 \text{Mn}^{2+} (aq) + 5 \text{S}_2\text{O}_8^{-2} (aq) + 8 \text{H}_2\text{O} (aq) \rightarrow 2 \text{MnO}_4^{-} (aq) + 10 \text{SO}_4^{-2} (aq) + 16 \text{H}^+ (aq)
\]

Absorbance is a measure of the amount of light absorbed by a solution; the darker the solution, the higher the absorbance. Colored solutions selectively absorb some wavelengths (colors) of light, while allowing others to pass through as you saw in the first lab. The permanganate appears purple because it allows red and blue light to pass, absorbing light in the green and yellow ranges.
The wavelength of light most efficiently absorbed (highest absorbance) by the compound is $\lambda_{\text{max}}$; this is, generally the best wavelength to use for measurements. Higher concentrations appear darker in color because they absorb more of the light. The absorbance follows Beer-Lambert’s Law

$$A = \varepsilon bc$$

where $A$ is the measured absorbance,
$\varepsilon$ is a constant and is determined from a Beer-Lambert plot (absorbance vs. conc.),
$b$ is the path length of the sample cell (cm) and
$c$ is the concentration of the sample (moles/liter).

By using a set of standards (solutions of different but known concentrations) a Beer-Lambert plot can be made. A Beer-Lambert plot of $A$ vs. concentration should be linear. This relationship some times fails if the concentration gets too high (because there is practically no light making it through the solution.)

The concentration of an unknown solution can then be determined graphically by measuring its absorbance and comparing it to a standard plot (or using the experimentally determined $\varepsilon$ value.)

**Sample Beer’s Law Plot**

![Beer's Law Plot](image)

**Prelab Assignment**

Write a purpose for this lab in your lab notebook.

Also, determine the exact concentrations of KMnO$_4$ that you will use to create your Beer’s Law plot (remember a solution of approximately $6.25 \times 10^{-4}$ M will be provided.) Calculate the dilutions necessary to make your concentration using volumetric glassware. Calculate the weight of disodium EDTA necessary to create 100 mL of your
standard EDTA solution.

**The Experiment**

You will use three different methods to determine the concentration of the MnSO₄ in the unknown solution. During one week, you will use both evaporation and titration with EDTA. During the other week you will use spectroscopy to determine the concentration of the unknown. Labs in C-7 will use the evaporation and titration methods in the first week and the spectroscopy in the second week. Labs in C-6 will undertake the spectrophotometric determination the first week then evaporation and titration the second week.

**Procedure**

**Part 1: Evaporation**

For this portion of the lab you should work with a partner. In this part of the experiment, you will use a steam bath to evaporate two samples of the manganese (II) sulfate solution. To set up the steam baths, fill two 150 ml beakers approximately 3/4 full with water and heat on a hot plate until the water boils gently.

**Preparation of Evaporation dish**

Meanwhile you can prepare two evaporating dishes to be used to evaporate the sample over the steam bath. The dishes must be dried to constant weight before using. To do so, clean and dry an evaporating dish and place it on a wire gauze resting on an iron ring. Heat the dish with your Bunsen burner until all the condensed moisture has been driven off. This should take about 5 minutes. Allow the dish to cool to room temperature and weigh it. Do this by using crucible tongs to handle the dish and a wire gauze to support it. This will prevent you getting oil on it from your fingers. Repeat the heating process until your weight is constant to ±0.005 g indicating that all the moisture has been removed.

**Evaporation and drying of sample**

Remove the covers and pipet 5.00 ml of your sample into each of the dishes. Note that for the best accuracy, you should do this using a volumetric pipet. Your LA will demonstrate to you the proper procedure for this. Place them on the steam bath (on the hot plate) and heat uncovered until dry.

Remove the evaporating dishes from the steam bath and place each of them on a clay triangle. Heat gently, uncovered, for a few minutes with the Bunsen burner to remove excess moisture. If material begins to spatter, immediately cover the dish with a watchglass of known mass.

After heating gently, place the watchglass on the dish and heat strongly for about 5 minutes. Remove the flame and allow the dishes to cool, then weigh. Repeat the process...
of heating over the burner, keeping the dish covered, cooling and weighing until constant weight is achieved (indicating that all the moisture has been removed.)

Using the Data
Calculate the weight of solid remaining and the concentration of the solution. Remember that you are trying to find the concentration in moles/liter of solution. You should calculate the average concentration of the manganese (II) sulfate solution from the two samples and be sure to show the range of values in your report. If you find that the two values are different by more than 5% you should repeat the process at least once more.

Part 2: Titration of EDTA
For this portion of the lab, you should work with a partner.

Preparation a dilute manganese (II) sulfate solution. Prepare a dilute solution of the manganese (II) sulfate solution by pipeting 1.00ml of the original unknown solution into a 100 ml volumetric flask and diluting to volume with distilled water. (Your LA will show you the appropriate technique for using a volumetric flask.) Transfer the solution to your sample bottle. Label the bottle with your name, date and identify the contents. This diluted solution will also be used in the third part of this experiment so be sure to save what is left. (If you already prepared your solution for part 3, then you will use that solution)

Note that the concentration of this solution ("dilute manganese unknown") is 1/100 the concentration of the original unknown.

Preparation of a standard EDTA solution. Prepare 100 ml of approximately 0.01 mol/L standard EDTA solution by accurately weighing a sample of disodium EDTA (Na₂C₁₀H₁₄N₂O₈·2H₂O M.W. = 372.24 g/mole). Record the actual weight. Quantitatively transfer the EDTA to a 100 ml volumetric flask. Add approximately 1 ml of concentrated ammonia and dilute to about 80 mL with distilled water. Be sure the EDTA is completely dissolved and thoroughly mixed. Dilute to exactly 100.00 mL.

Calculate [EDTA] (remember that this should be approximately 0.01 mol/L)

Preparation of analytical sample
Pipet 10.00 ml of the EDTA solution into a 250 ml Erlenmeyer flask. Add the following (volumes are approximates):
- 5 ml of pH = 10 buffer, already prepared
- 1 ml triethanolamine
- 5 ml 5% ascorbic acid solution, already prepared
- 20 ml distilled water

Add Eriochrome Black T indicator until the solution is a medium to dark blue color. Fill a buret with the dilute manganese unknown. Titrate the EDTA sample to the endpoint
where the solution changes to a red color. Record the volume of dilute manganese unknown solution required to reach the endpoint.

Repeat the titration procedure on 2 additional 10.00 ml samples of your EDTA solution.

*Using the Data*

At the endpoint of the titration, the moles of EDTA are equal to the moles of Mn\(^{2+}\) in solution. Calculate the moles of EDTA in the solution. From this, calculate the concentration of the diluted manganese unknown and then the concentration of your original unknown manganese (II) sulfate solution (remember that you diluted the original solutions). To do this you can use the following relationship:

\[ M_1V_1 = M_2V_2 \]

Where M represents the concentration and V represents the volume. Since the concentration times the volume should give you the amount of material present, then this simply indicates that the amount of material in the sample did not change during the dilution process.

Calculate the average concentration of the original manganese (II) sulfate solution using the results from this method. Calculate the range (spread in concentration) of your values.

### Part 3: Spectrophotometric Determination

*In part 3 of this experiment, pairs of students will be responsible for preparing their own unknown solutions as described in the following section A. The instructions for sections B through C will be carried out by groups of 3-5 students. The data obtained by each group for the standard solutions will be shared by each member of that group, though every pair will determine the concentration of their own unknown solutions.*

#### A. Preparation of an Unknown Permanganate Solution

A sample of dilute manganese unknown will be converted to a permanganate solution by the following procedure.

Pipette 1.00 ml of the dilute manganese unknown (from part B) into 3 separate beakers. [If you have not done part 2 yet, then prepare the dilute solution according to those directions. Be sure to label and save this.] To each, add approximate amounts of each of the following:

- 50 ml distilled water
- 10 ml 3M sulfuric acid
- 1 ml 5% silver nitrate solution, AgNO3, already prepared

Heat solution strongly but do not boil. Then add:

1 g ammonium persulfate, \((NH_4)_2S_2O_8\)
Heat (DO NOT BOIL) for an additional minute until the solutions turns a violet-purple color. Remove the beaker from the hot plate, and let the solution stand for 1 minute then cool under the tap. (Boiling too long results in decomposition of the excess persulfate and subsequent loss of color; cooling too slowly has the same effect). When the solution is cool, transfer the liquid quantitatively to 100 ml volumetric flasks and dilute to the mark with distilled water. Keep in mind that quantitatively means that you will need to get as much as possible out of the beaker. You may want to rinse the beaker a couple of times with 5 mL of distilled water and add each portion to the volumetric flask. Label as permanganate X, Y and Z.

Note that the $[\text{MnO}_4^-]$ is 1/100 the concentration of the "diluted manganese unknown", or $1/100 \times 1/100 (= 1/10,000)$ the concentration of the original manganese (II) sulfate unknown solution.

**B. Determination of $\lambda_{\text{max}}$**
You may use the Ocean Optics USB2000 for the spectrophotometric determination. You should use the provided solution of permanganate to determine the $\lambda_{\text{max}}$ for permanganate. You should scan at least the region between 400 and 800 nm to find the $\lambda_{\text{max}}$.

The spectrometers you will need to calibrate the instrument using a blank cuvet (containing water) before you will be able to collect the permanganate solution data (Your LA will demonstrate how to do this. There will also be instructions present in the lab.)

Find the $\lambda_{\text{max}}$ either directly from the graph of the full spectrum. The $\lambda_{\text{max}}$ should be used to measure the absorbance of all the solutions (both standards and unknowns.)

**C. Preparation of Beer-Lambert plot.**
You should prepare a Beer-Lambert plot to guarantee that the MnO$_4^-$ follows Beer’s Law at this concentration. First, prepare a working stock solution by dilute the stock solution by a factor of 10. Label this solution. Using the working stock permanganate solution with known concentration you should as accurately as possible (i.e. using volumetric glassware) create solution with at least 5 different known concentrations (for example you might use the working stock solution, a solution that is half as concentrated, one that is 1/3rd as concentrate, on 1/4th as concentrated…) [As you are doing this may be interesting to compare the solutions you made to those made by another group. Do they give the same absorption?] Plot the absorbance of each solution against the concentration to determine the best linear trendline. Then calculate the $[\text{MnO}_4^-]$ for each of your unknown solutions X, Y and Z using the equation for the trend line to convert between absorbance and concentration. **Print a copy of your plot, affix it to your notebook and have it graded before you leave the lab.**

Find your average concentration of your original manganese(II) sulfate unknown using the three results from this method as well as the range.
Report
This week’s report should include the title page, abstract, procedure, data presentation (results and calculations) and discussion. The focus of this week’s report will be the abstract, data presentation (results and calculations) and discussion. It should be written with your partner (not your full group of four from the spectroscopy portion). In your discussion you should thoughtfully addressing the following three issues listed below. Your report grade will depend on both the completeness and accuracy. If you believe that you have any unreliable data, be sure to address why you feel it is not accurate.

Issues
A. Compare the three methods based on the following criteria:
   - Precision of results
   - Simplicity of procedure and skill required
   - Required time
   - Possible sources of error and their effects on [MnO₄⁻] found
   - Equipment and reagent requirements

B. Report your data and calculations for each method. You should also include the full spectrum of the permanganate as well as your plot to demonstrate that the permanganate follows Beer’s Law. Report the concentration of manganese (II) sulfate solution and the range found using each of the three methods.

Considering your answer in part A of your report, what is your best estimate of the actual concentration of manganese (II) sulfate in your sample?

C. 1. Suppose your original unknown contained some dissolved NaCl in addition to the MnSO₄. NaCl is colorless, nonvolatile, and does not react with EDTA.
   a. What problems (if any) would this cause in each of the three methods?
   b. Explain whether each method would give a result which was too low, too high, or (Goldilocks' favorite) "just right".
2. Repeat problem #1, except the additional compound is BaCl₂, instead of NaCl. BaCl₂ is colorless, nonvolatile, and reacts with EDTA in a 1:1 ratio.
3. Repeat problem #1, except the additional compound is ethyl alcohol, instead of NaCl. Ethyl alcohol is colorless, volatile, and does not react with EDTA.
4. Repeat problem #1, except the additional substance is grape juice, instead of NaCl. Grape juice is purple, volatile, and does not react with EDTA.
5. [BONUS] If all four (NaCl, BaCl₂, ethyl alcohol, and grape juice) were present along with the MnSO₄, would any of the methods work? Can you devise one that would?

Chemicals
MnSO₄, disodium EDTA, concentrated ammonia, pH 10 buffer solution, triethanolamine, 5% ascorbic acid solution, Eriochrome Black T indicator, 3M sulfuric acid, 5% silver nitrate solution (AgNO₃), ammonium persulfate (NH₄)₂S₂O₈, KMnO₄ solution
Chemical Disposal
Dispose of all EDTA, permanganate or silver containing solution in waste container. Solid MnSO₄ can be dissolved and added to the solution waste.

Equipment
Clay triangles, Evaporating Dishes, Bunsen burners, Hot plate, Wire Gauze, Buret, volumetric flasks, volumetric pipets, Cuvettes, OceanOptics USB2000

References
Frederick C. Sauls and Maria L. Pavco Chemistry 113L Laboratory Manual, King’s College, Willkes-Barres, PA, 1996.