

## Experiment 10b: Measuring Manganese in Steel with Standard Addition

CH2250: Techniques in Laboratory Chemistry, Plymouth State University

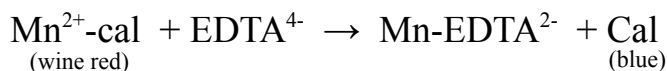
Adapted from "27.  $\text{Mn}^{2+}$  Standardization by EDTA Titration," and "28. Measuring Manganese in Steel by Spectrophotometry with Standard Addition " *Experiments To Accompany Exploring Chemical Analysis, 4th Edition*, Daniel C. Harris (2008), available at <http://www.whfreeman.com/exploringchem4e>. Originally taken from S. P. Perone, J. Pesek, C. Stone, and P. Englert, *J. Chem. Ed.*, **75**:1444 (1998).

Suggested reading for background information: Section 5.3, *Exploring Chemical Analysis, 4th Edition*, Daniel C. Harris (2008).

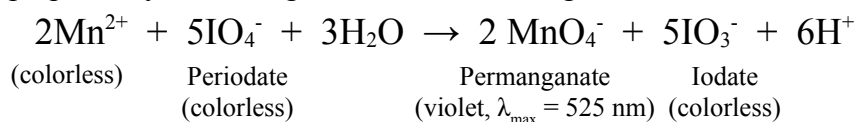
### Introduction:

Sometimes in spectroscopic analysis, species present in the matrix absorb in the region of the analyte of interest. This background interference can be overcome by the use of standard addition to develop the calibration curve. In this technique, the calibration curve is not made by a series of pristinely prepared standards, but instead, the standard is added in increasing amounts to a series of the unknown. Each sample is then diluted to the same final volume. In this way, each "standard" contains the same amount of the interfering background substance, allowing it to be subtracted out. The actual concentration of unknown is found by extrapolating the line back to the point of zero absorbance (Figure 1).

Steel is an alloy of iron that typically contains ~0.5 wt% Mn plus numerous other elements. In this experiment, samples of steel are analyzed for their manganese content. A standard solution of  $\text{Mn}^{2+}$  is prepared and standardized by EDTA titration. The titration is observed using calmagite indicator, which is *Figure 1* wine red when bound to a metal ion, but blue when unbound. EDTA displaces the indicator as shown in the equation :



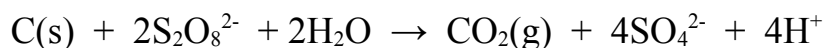
Steel samples are prepared by dissolving in acid and oxidizing their Mn to the violet permanganate ion:



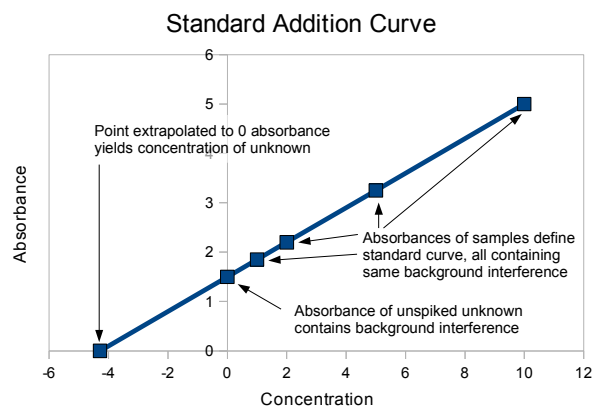
*(Preparation of steel samples will be done during a previous lab time.)*

Absorbance is measured with a spectrophotometer and the concentration of Mn in the unknown sample is calculated based on the change in absorbance due to the standard addition.

When steel is dissolved in hot nitric acid, the iron is converted to Fe(III). Spectrophotometric interference in the measurement of  $\text{MnO}_4^-$  by Fe(III) is minimized by adding  $\text{H}_3\text{PO}_4$  to form a nearly colorless complex with Fe(III). Interference by most other colored impurities is eliminated by subtracting the absorbance of a reagent blank from that of the unknown. Carbon from the steel is eliminated by oxidation with peroxydisulfate ( $\text{S}_2\text{O}_8^{2-}$ ):



**Equipment:** Read through the procedures and make a list of the equipment you will need.



### Safety Considerations:

- Manganese, particularly permanganate ( $\text{MnO}_4^-$ ) is toxic and must be disposed of properly.
- Do not breathe dust from  $\text{NH}_3\text{OH}^+\text{Cl}^-$ . Avoid contact with skin and eyes.
- Read through the procedures and note any other safety considerations.

### Procedure:

#### **A. Pre-Lab Considerations**

1. You will previously have prepared the steel sample in Experiment 10a. Be sure to reference the page numbers of that experiment in the beginning of your lab write-up for this this part.
2. The experimental portion of this lab has numerous solutions, which can make the final analysis confusing if you are not organized. As part of your pre-lab Procedure, draw an "experimental sketch" showing all the solutions with labels and all the relevant details you know. This may include molecular contents, volumes, concentrations, number of moles, and how it is to be made (e.g., the mass or volume of something added to the flask).

#### **B. Preparation of $\text{Mn}^{2+}$ Standard**

1. Prepare Stock Standard containing  $\sim 1.0$  mg Mn/mL ( $\sim 0.018$  M) by dissolving  $\sim 0.15$  g  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  in a 125 mL Erlenmeyer flask with 50 mL water delivered from a graduated cylinder. *Note that you do not need to measure out the exact mass of  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ , because you will titrate this solution below to find the exact concentration.*
2. Prepare Diluted Standard: Rinse a clean 25-mL pipet several times with small volumes of  $\text{Mn}^{2+}$  Stock Standard and *discard the washings into a chemical waste container*. Then pipet 25.00 mL of Stock Standard 1.0 into a 100-mL volumetric flask. Add 0.40 g of solid hydroxylamine hydrochloride ( $\text{NH}_3\text{OH}^+\text{Cl}^-$ ) to the flask, and swirl to dissolve the solid. Add  $\sim 50$  mL of water and swirl to mix the contents. Dilute to the mark with water, set the cap firmly in place, and invert several times to mix the solution. *This solution contains  $\sim 0.0045$  M  $\text{Mn}^{2+}$ .* (The reducing agent, hydroxylamine, maintains manganese in the +2 state).
3. Fill a buret with the standardized EDTA solution provided. Note the exact concentration of the solution.
4. Perform a quick "throw away" titration to find the approximate volume of titrant needed: Rinse a 10-mL pipet several times with small volumes of the Diluted Standard. Pipet 10 mL of this  $\text{Mn}^{2+}$  solution into a 125-mL Erlenmeyer flask. Add 10 mL of pH 9.7 buffer (by graduated cylinder), and 2 drops of calmagite indicator. Titrate to the end point, when the color changes from wine red to blue. Do a rough calculation of the amount of titrant needed for the careful titrations, *noting that you will use 2.5 times the amount of analyte in your careful titrations.*
5. Perform two or three (if the first two are not sufficiently close) careful titrations in a similar manner (except that the volumes are multiplied by 2.5!): Rinse a 25-mL pipet several times with small volumes of the Diluted Standard. Pipet 25 mL of this  $\text{Mn}^{2+}$  solution into a 125-mL Erlenmeyer flask. Add 25 mL of pH 9.7 buffer (by graduated cylinder) and 3-5 drops of calmagite indicator. Titrate to the end point, when the color changes from wine red to blue.
6. Properly dispose of all waste solutions and rinses containing  $\text{Mn}^{2+}$ .



### C. Preparing Standard Additions Solutions

1. Pipet 25.00 mL of liquid from the Sample Solution (prepared in Lab 10a) into each of four clean, dry 100-mL beakers designated "blank," "unknown," "standard addition 1," and "standard addition 2." *Save your remaining Sample Solution for use when you will repeat this analysis.*
2. Add 5 mL of 85 wt% H<sub>3</sub>PO<sub>4</sub> (from a graduated cylinder) into each beaker.
3. Add Stock Standard (using autopipettes) and solid KIO<sub>4</sub> as follows:

Beaker	Volume of Mn <sup>2+</sup> Stock 0.1 (mL)	Mass of KIO <sub>4</sub> (g)
Blank	0	0
Unknown	0	0.4
Standard addition 1	0.4	0.4
Standard addition 2	0.8	0.4

4. Boil the unknown and standard addition beakers gently for 5 min to oxidize Mn<sup>2+</sup> to MnO<sub>4</sub><sup>-</sup>. Continue boiling, if necessary, until the KIO<sub>4</sub> dissolves. You may need to add 5-10 mL of H<sub>2</sub>O to promote dissolution.
5. Quantitatively transfer the contents of each of the beakers into 50 mL volumetric flasks (label these flasks!). Wash each beaker many times with small portions of water and transfer the water to the corresponding volumetric flask. Dilute to the mark with water and mix well. *You will likely only have two 50 mL volumetric flasks, so make two solutions, transfer them to clean, dry, labeled beakers or bottles, wash the flasks, and make the other two solutions.*

**SAVE YOUR REMAINING SAMPLE SOLUTION FROM EXPERIMENT 10A** for use in the week of May 1, when you will repeat this analysis.

### D. Spectroscopic Measurement

1. Calibrate a Spec 20 colorimeter at 525 nm.
2. Measure the absorbances of the four Standard Additions Solutions. *Remember to rinse the cuvet a few times with small quantities of the solution to be measured and discard the rinses before taking the absorbance.*

**SAVE YOUR REMAINING SAMPLE SOLUTION FROM EXPERIMENT 10A** for use in the week of May 1, when you will repeat this analysis.



## Analysis

Read through the analysis questions below and setup tables to best organize your work.

### **A. Preparation of Standard Solution**

1. From the molarity and volume of standard EDTA required for titration, calculate the moles of EDTA required to titrate the 25 mL of Diluted Standard for each of the careful titrations you performed (Step B5). Calculate the mean.
2. From the average moles of EDTA, calculate total moles of  $\text{Mn}^{2+}$  in the 100 mL of Diluted Standard (B2), and then the molarity of the Diluted Standard. Your answer should be close to 0.0045M (but of course you will have more sig figs).
3. From the molarity of the Diluted Standard, calculate the molarity of  $\text{Mn}^{2+}$  in the Stock Standard (B1). Your answer should be  $\sim 0.018$  M. Express your answer with an appropriate number of significant digits.

### **B. Spectroscopic Determination of Mn in Steel**

1. From the known concentration of the Mn Stock Standard, calculate the moles of extra Mn added to the Standard Addition 1 and 2 solutions.
2. Use your answer from B1 to calculate the concentration of added Mn in Standard Addition 1 and 2 solutions.
3. Calculate the corrected absorbances for the Unknown and the Standard Addition 1 and 2 solutions by subtracting the absorbance of the Blank from them.
4. Use a spreadsheet to plot a Standard Addition Curve of corrected absorbance (Question B3) versus concentration of added Mn for the Unknown and Standard Addition 1 and 2 (Question B2). *Note the concentration of added Mn in the Unknown is 0.* Print a copy of this graph and include it in your notebook.
5. Calculate the slope and intercept for the Standard Addition Curve. Provide the equation of the best-fit line.
6. Calculate the concentration of Mn in the Unknown by extrapolating the best fit line back to the x-intercept (point where  $y = 0$ ).
7. From the concentration of the Unknown, calculate the concentration of the Sample Solution.
8. From the concentration of the Sample Solution, calculate the weight percent of Mn in the original steel sample (you will need to refer to your data from Lab 12a for this). *Next to your answer in your notebook, **NOTE THE SAMPLE NUMBER OF THE STEEL SAMPLE.***

## Homework Problems

The following homework problems from your book are suggested to help you improve your understanding of the standard additions method: Ch 5: 16, 17, 18, 20

## Report

You will NOT complete a standard Notebook Report for this lab. Instead you will prepare a draft of the report after the first time you perform this analysis and a final version of the report after the second time. See “Writing the Formal Lab Report” on the **course website** for more information about the draft and the final version. Especially note that the draft does NOT contain all portions of the final report!

