Simultaneous Determination of Chromium and Manganese in a Sample of Steel

I. Required Reading

In addition to reading this project description and answering questions in the prelab section, you should read Chapter 24C and Chapter 26 of the course textbook. Also review Example 26-3, which deals with absorbance of a mixture of two absorbers. Review Chapter 8C, which discusses standard calibration.

II. Introduction

Steel is an alloy consisting principally of iron but with many other metallic components present. The exact metallic composition of steel depends on the purpose for which the steel is intended. Stainless steel, for example, has a rather different composition from armor plate. Many types of steels contain chromium and manganese. This experiment is intended to illustrate how the chromium and manganese content in steel can be determined using spectrophotometric methods. In this method, Cr and Mn are oxidized to Cr$_2$O$_7^{2-}$ and MnO$_4^-$, respectively, with a strong oxidizing agent. The absorption spectra of these two highly colored anions overlap significantly, and it is not possible to observe absorbance due to one or the other anion in the visible range at any wavelength where the method has adequate sensitivity. This experiment illustrates how one can extract the separate concentrations of Cr and Mn from spectrophotometric measurements at wavelengths where both Cr$_2$O$_7^{2-}$ and MnO$_4^-$ absorb.

The approach relies on a direct application of Beer’s law to a mixture of two absorbing species. For a given species $i$ the wavelength-dependent absorbance $A_i(\lambda)$ is given by

$$A_i(\lambda) = \varepsilon_i(\lambda)bC_i$$

(1)

where $\varepsilon_i(\lambda)$ is the wavelength-dependent molar extinction coefficient of species $i$, $b$ is the pathlength of the measuring cell in cm, and $C_i$ is the molar concentration of the absorbing species $i$. Since absorbance is dimensionless, the resulting conventional units of $\varepsilon_i(\lambda)$ are L mol$^{-1}$cm$^{-1}$.

This experiment uses simultaneous spectrophotometric determination of two analytes in a solution. If Beer’s law holds for both species the absorbances should be additive:

$$A(\lambda_1) = A_1(\lambda_1) + A_2(\lambda_1)$$
$$A(\lambda_2) = A_1(\lambda_2) + A_2(\lambda_2)$$

(2)  (3)

where $A(\lambda_i)$ is the total measured absorbance of the two species at wavelength $\lambda_i$ and $A(\lambda_j)$ is the total measured absorbance of the two species at wavelength $\lambda_j$. The subscripts 1 and 2 designate the two different substances, and $\lambda_1$ and $\lambda_2$ refer to two appropriately selected wavelengths at which absorption arises principally from substances 1 and 2, respectively.

For consistency in reporting, we will identify the compounds as follows:

- Cr$_2$O$_7^{2-}$ = substance 1
- MnO$_4^-$ = substance 2

Please stick with these definitions in your report!

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For maximum sensitivity these wavelengths are selected to coincide with the respective absorption maxima of the two solutes. Because the absorption spectra overlap in the present case, substance 1 absorbs strongly at the wavelength $\lambda_1$ but also contributes to absorbance at $\lambda_2$, and substance 2 absorbs strongly at $\lambda_2$ and also has some absorbance at $\lambda_1$. Substituting for the terms on the righthand side of equations (2) and (3) using equation (1) we obtain:

$$A(\lambda_1) = b \times \{\varepsilon_1(\lambda_1)C_1 + \varepsilon_2(\lambda_1)C_2\}$$  \hspace{1cm} (4)$$

$$A(\lambda_2) = b \times \{\varepsilon_1(\lambda_2)C_1 + \varepsilon_2(\lambda_2)C_2\}$$  \hspace{1cm} (5)$$

The pathlength $b$ can be readily determined with a caliper. Values of the molar extinction coefficients at any wavelength can then be deduced, respectively, from measurements of the absorbance of solutions of known concentration containing individual substances 1 and 2 using equation (1). Therefore, following measurement of the absorbances $A(\lambda_1)$ and $A(\lambda_2)$ of the mixture at wavelengths $\lambda_1$ and $\lambda_2$, we will have two equations for two unknowns, $C_1$ and $C_2$. These two simultaneous equations are then easily solved to obtain the unknown concentrations.

### III. Determination of Extinction Coefficients of Cr$_2$O$_7^{2-}$ and MnO$_4^-$

In this step you will measure absorption spectra and determine extinction coefficients for Cr$_2$O$_7^{2-}$ and MnO$_4^-$. Prepare the following stock solutions using nanopure water: 100 mL of 0.010 M K$_2$Cr$_2$O$_7$ and 500 mL of 0.0020 M KMnO$_4$. You do not really need this much KMnO$_4$ solution, but you want to be able to weigh out enough of the salt to get at least four digit precision in your weighing accuracy. It is not important that the concentrations be exactly those stated above, but you must know the concentrations exactly. Use these stock solutions of Cr$_2$O$_7^{2-}$ and MnO$_4^-$ to prepare additional solutions with the following approximate (but accurately known) concentrations:

- K$_2$Cr$_2$O$_7$: 0.0010 M, 0.00050 M, 0.00020 M
- KMnO$_4$: 0.00040 M, 0.00020 M, 0.00010 M

Follow a dilution procedure that allows you to use your calibrated pipettes to deliver the stock solution and your volumetric flasks to contain the diluted stock solution. Your 100 mL and 250 mL volumetric flasks should be convenient for the purposes at hand. Your group will need to pool your supply of volumetric flasks together in order to have enough of them for this job.

Choose a pair of measuring cells and stick with this pair, using one consistently for the solution and the other consistently for the reference. This prevents errors arising from small differences in the path lengths of the spectrophotometer cells. If the path length of your cells is not specified on the packaging, measure the path lengths as well as you can. If you stick with a single set of cells, it will turn out that the path length is not really needed, but you will want to know it approximately.

Instructions for operating the spectrophotometer can be found on the lab bench near the instrument. Your TA can also help you if you have questions about the operation of the instrument. Before you do any measurements with the UVVIS spectrometer you have to baseline-correct it. Fill your sample cell and reference cell with nanopure water. Press “baseline” (not “Autozero”). When the correction procedure is finished, the spectrometer should measure zero absorbance for all wavelengths when both cells are filled with water. Note: you
many need to repeat the background correction later if you notice that your spectrometer drifted, and started registering non-zero absorbance when your cells are filled with nanopure water.

Choose one of the diluted \( \text{Cr}_2\text{O}_7^{2-} \) solutions and one of the diluted \( \text{MnO}_4^- \) solutions and measure the absorption spectrum of each ion throughout the range of 300 – 700 nm. Print the absorption spectra and locate the absorption maxima within the visible range.

Find two appropriate wavelengths for your measurements using the following criteria. The wavelengths of the absorption maxima you choose will be the wavelengths \( \lambda_1 \) and \( \lambda_2 \) that enter into equations (4) and (5).

1. The first wavelength should have strong \( \text{Cr}_2\text{O}_7^{2-} \) absorption and weak \( \text{MnO}_4^- \) absorption
2. The second wavelength should conversely have strong \( \text{MnO}_4^- \) absorption and weak \( \text{Cr}_2\text{O}_7^{2-} \) absorption
3. Your most concentrated solutions of \( \text{MnO}_4^- \) and \( \text{Cr}_2\text{O}_7^{2-} \) should not have absorbance in excess of 1 at either wavelength

If an ion has more than one maximum, it is not always best to select the strongest one. This analysis is based on using the visible absorption bands responsible for the colors of these ions even if these are not the strongest bands you can observe using the UV-VIS instrument. It is important that your measured absorbance does not exceed 1 absorbance units in order to prevent deviations from the Beer’s law.

Measure the absorbances of your three diluted solutions of \( \text{Cr}_2\text{O}_7^{2-} \) and \( \text{MnO}_4^- \) at wavelengths \( \lambda_1 \) and \( \lambda_2 \). You must measure the absorbance of each ion at each wavelength (12 measurements altogether). Plot the measured absorbances as follows:

- \( A_1(\lambda_1) \) versus \( C_1 \). The points should fall on a straight line with a slope of \( b\varepsilon_1(\lambda_1) \).
- \( A_1(\lambda_2) \) versus \( C_1 \). The points should fall on a straight line with a slope of \( b\varepsilon_1(\lambda_2) \).
- \( A_2(\lambda_1) \) versus \( C_2 \). The points should fall on a straight line with a slope of \( b\varepsilon_2(\lambda_1) \).
- \( A_2(\lambda_2) \) versus \( C_2 \). The points should fall on a straight line with a slope of \( b\varepsilon_2(\lambda_2) \).

Determine the standard deviation for each slope using the least squares method described in Chapter 8C of the textbook. Is the Beer-Lambert Law valid? In order to extract values of \( \varepsilon_\lambda(\lambda) \) for each substance, divide the slopes you obtain by the pathlength \( b \). You will be reporting these values in your report.

To test the additivity assumption made in writing equations (2) and (3), make mixtures of your 0.0010 M \( \text{Cr}_2\text{O}_7^{2-} \) solution and your 0.0004 M \( \text{MnO}_4^- \) solution in the proportions 1:5, 1:1, and 5:1. Measure the absorbance of these mixtures at \( \lambda_1 \) and \( \lambda_2 \). Note that these mixtures need to be made accurately for this purpose so that you know the concentrations exactly.

**IV. Dissolution of the Unknown for Analysis**

1. Accurately weigh the entire content of your steel unknown, place it into a 25 mL Erlenmeyer flask, add 3 mL of nanopure water, and carefully add 1 mL of concentrated \( \text{H}_2\text{SO}_4 \). Also add 1 mL of 85 percent \( \text{H}_3\text{PO}_4 \) if tungsten is present (your TA will tell you if your sample has tungsten). Cover the top of the Erlenmeyer flask with a watchglass to prevent splattering of liquid during subsequent boiling.

2. Boil gently in a fume hood using a hot plate until the reaction evolving \( \text{H}_2 \) subsides (clamp your beaker to keep it steady). Then carefully add 1 mL of concentrated \( \text{HNO}_3 \) in several small portions; the reaction can be quite vigorous, so make your additions gingerly. If carbonaceous (black) residue persists, add 0.5 mL more of concentrated \( \text{HNO}_3 \). Repeat the \( \text{HNO}_3 \) treatment, if necessary, until the carbonaceous material is all consumed. Then boil the mixture
until dense fumes of SO$_3$ appear in the flask \textit{(do not boil dry!). Cool, dilute carefully with about 10 mL of nanopure water, and boil until all salts have dissolved. Cool the resulting solution.}

V. Oxidation of the Cr and Mn Components
1. Quantitatively transfer the entire amount of the light green sample solution into a 250 mL Erlenmeyer flask. Add about 50 mL water. Add 5 mL of concentrated H$_2$SO$_4$, 5 mL of 85% H$_3$PO$_4$, and 1-2 mL of 0.1 M AgNO$_3$ solution. The latter solution will be provided for you; do not let this, or any of the other reagents, contact your skin.

2. Dilute to about 80 mL with nanopure water and add 5 g of K$_2$S$_2$O$_8$ (potassium persulfate). Swirl the contents of the flask until most of the salt has dissolved, and heat to boiling. Keep at the boiling point for 5-7 minutes. Cool slightly, and add 0.5 g of pure KIO$_4$ (potassium periodate). Again, heat to boiling and maintain at the boiling point for about 5 minutes. Since both Cr$_2$O$_7^{2-}$ and MnO$_4^-$ are themselves strong oxidizing agents, powerful oxidizers are required to oxidize Cr and Mn to their high oxidation states in these ions. Silver ion catalyzes the oxidation of Cr and Mn by persulfate.

3. Cool, transfer quantitatively to a 100 mL volumetric flask, and dilute to the mark with nanopure water.

VI. Measurement of the Concentrations of Cr$_2$O$_7^{2-}$ and MnO$_4^-$ in the Unknown Solution
Measure the absorbances of the solution prepared in step III above at $\lambda_1$ and $\lambda_2$ as required to supply values for the lefthand side of equations (4) and (5). If the measured absorbances at $\lambda_1$ and $\lambda_2$ are considerably larger than the absorbances measured for your standard samples (and standard sample mixtures), you should dilute the unknown to bring the measured absorbances into the range used to determine the several values of $\varepsilon_i(\lambda)$ that you measured. Otherwise, you run the risk of being outside the Beer-Lambert range. If you make such a dilution, do not forget to include it in your final determination of the amounts of Cr and Mn in your steel sample. There are other dilutions to take into account as well.

VII. What to Submit in Your Report
1. As usual, turn in your prelab at the beginning, your duplicate copies of all the notebook pages at the end of the laboratory session. Remember: your lab will count for nothing if your lab notebook pages are not submitted or contain meaningless information. Be sure to include your name and student number, names of your group members, and the project title on the title page.

2. Important: At the end of the lab, you will be required to show your TA printed copies of all UV spectra you collected. After your TA approves your results, you should take the printouts with you because you will need them for you report preparation. Include them with your report. \textbf{You only need one set of print outs for the whole group; you do not need one for every student in the group.}

3. Generate and include in your report plots of absorbances of your diluted standard solutions vs. concentrations, with linear fits included to show to which extent Beer’s law is valid. Show how you obtained your extinction coefficients from these plots. Provide a table of extinction coefficients that you measured in the following format. Include the units. Standard deviations for $\varepsilon_i(\lambda)$ and $\varepsilon_1(\lambda)$ should be calculated using methods described in Chapter 8C.

<table>
<thead>
<tr>
<th>Wavelength</th>
<th>$\varepsilon_1(\lambda)$</th>
<th>Standard deviation for $\varepsilon_1(\lambda)$</th>
<th>$\varepsilon_2(\lambda)$</th>
<th>Standard deviation for $\varepsilon_2(\lambda)$</th>
</tr>
</thead>
</table>

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4. Discuss the results of your additivity test. Compare the predicted values of absorbance based on the measured extinction coefficients and measured ones.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Predicted $A(\lambda_1)$</th>
<th>Measured $A(\lambda_1)$</th>
<th>Predicted $A(\lambda_2)$</th>
<th>Measured $A(\lambda_2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5:1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1:1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1:5</td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

5. Solve equations (4) and (5) and determine the concentrations of Cr$_2$O$_7^{2-}$ and MnO$_4^-$, in the unknown sample. Taking into account both the chemistry of the analysis and the dilutions made, convert these results to weight percent Cr and weight percent Mn in the steel sample issued to your group. Report these weight percents along with their standard deviations. You will need to use propagation of errors to do these calculations.

**Note on Interferences:** Other components in the steel may contribute to the absorbances at $\lambda_1$ and $\lambda_2$. Unless these interferences are taken into account, you may overestimate the amounts of Cr and Mn using the procedure outlined here because the present treatment assumes that all of the absorbance comes from these two elements. Lingane and Collat (*Analytical Chemistry* 1950, 22, 166) discuss this issue and provide a correction table that permits taking into account the contributions from V, Co, Ni, and Fe. For example, steel containing 50% Fe will cause the Cr content calculated without any correction to be too large by 0.025%. Steel containing 5% Ni will cause the Cr content calculated without any correction to be too large by 0.020%. In neither case is there any significant interference with the Mn determination. In the most exacting measurements these interferences would need to be taken into account. But because the adjustments are generally negligible, as illustrated by the examples above, you are not required to make such corrections.