Experiment. Analysis of Manganese in Steel via UV-Vis Spectroscopy

Objective: Small quantities of manganese can be determined as highly colored permanganate ion. Potassium periodate is effective at oxidizing lower oxidation states of manganese to MnO_4^-, which exhibits a maximum absorbance at 525 nm.

Reaction : $2Mn^{2+} + 5IO_4^- + 3H_2O \leftrightarrows 2MnO_4^- + 5IO_3^- + 6H^+$

A reagent blank, consisting of the unoxidized sample, is used to compensate for other constituents in the sample that absorb at this wavelength. Large quantities of cerium(III) and chromium(III) interfere because they are oxidized by the periodate to cerium(IV) and $Cr_2O_7^{2-}$, both of which absorb at 525 nm. Ferric ion also absorbs at the measurement wavelength, but its interference is avoided by adding phosphoric acid, which reacts with the iron, converting it to a nonabsorbing complex ion.

Equipment		Chemicals	
Desciccator	Plastic storage bottle	$MnSO_4 \cdot H_2O$ (2g)	HNO_3 6M (150mL)
1-L Vol Flask	3-250 mL Elm Flask	$(NH_4)_2S_2O_8$ (3 g)	Na_2SO_3 (0.3 g)
25-mL Vol pipet	3-100ml Vol Flask	H_3PO_4 concentrated (45 mL)	KIO_4 (3.0 g)
3-125 mL beakers	5-mL Vol pipet		
1-10mL grad cylinder	3-50 mL Vol Flask		
Cuvette cells	Cary 50 Spectrophotometer		

Safety and Waste Disposal

Check all glassware for stress, stars, or fatigue before performing this experiment.
Use safety goggles, lab jacket, latex gloves for this experiment.

Discussion:.

Math Relationship

Calibration curves are usually used to determine the relation between signal and concentration in a chemical analysis. In cases where a calibration curve would be inappropriate and unreliable, *standard addition* or *internal standards* can be use.

In the method of standard addition, a known quantity of analyte is added to a sample and the increase in signal is measured. The relative increase in signal allows us to infer how much analyte was in the original speciemen. The key assumption is that signal is proportional to the concentration of analyte.

Standard addition is used when the sample matrix is <u>complex or unknown</u>. For example, a matrix such as blood has many constituents that you could not incorporate into standard solutions for a calibration curve. We add small volumes of concentrated standard to the unknown so that we do not change the matrix very much.

Suppose that a sample with unknown initial concentration $[X]_i$ gives a signal A_X where A might be the absorbance intensity, the detector current or voltage of an instrument or the area of a chromatogram signal Then a known concentration of standard S (a known concentration of analyte) is added to the sample and a signal A_{S+X} is observed. Because signal is proportional to analyte concentration, the following equation can be used

$$\frac{\text{Concentration of analyte in Unknown}}{\text{Concentration of analyte plus standard in mixture}} = \frac{\text{Signal from unknown}}{\text{Signal from mixture}}$$

Standard Addition Equation: $$\frac{[X]_i}{[X]_f + [S]_f} = \frac{A_x}{A_{s+x}}$$

Where $[X]_f$ is the final concentration of unknown analyte after adding the standard, and $[S]_f$ is the final concentration of standard after addition to the unknown. If we began with an initial volume Vo of unknown and added the volume Vs of standard with initial concentration $[S]_i$ the volume is V = Vo + Vs and the concentration from the above standard addition equation are

$$[X]_f = [X]_i * \left(\frac{V_o}{V}\right) \qquad [S]_f = [S]_i * \left(\frac{V_o}{V}\right)$$

Dilution factor   Dilution Factor

In this experiment, the amount of manganese in a steel sample will be determine by converting all the manganese in the steel to permanganate ion. The absorbance of the permanganate ion will be compared to the absorbance of a precalculated amount of permanganate standard. In this case the standard addition equation becomes:

$$\frac{A_{unk}}{A_{std+unk}} = \frac{[Mn^{+n}]_{unk}}{[Mn^{+n}]_{unk} + [Mn^{+n}]_{std}}$$

where $[Mn^{+n}]_{unk}$ is the concentration of manganese in the steel, and $[Mn^{+n}]_{std}$ is the concentration of manganese in the $MnSO_4$ standard. A_{unk} is the absorbance of the unknown and $A_{std+unk}$ is the absorbance of the manganese unknown and standard solution.

In the derivation below, $[Mn^{+n}]_{unk}$ is represented by [Mn]. Rearranging this equation for $[Mn]_{unk}$ leads to:

$$\frac{A_{unk}}{A_{std+unk}} = \frac{[Mn]_{unk}}{[Mn]_{unk} + [Mn]_{std}}$$

$$A_{unk}\left([Mn]_{unk} + [Mn]_{std}\right) = [Mn]_{unk} \bullet A_{unk+std}$$

$$A_{unk}[Mn]_{unk} + A_{unk}[Mn]_{std} = A_{unk+std} \bullet [Mn]_{unk}$$

$$A_{unk}[Mn]_{std} = A_{unk+std} \bullet [Mn]_{unk} - A_{unk}[Mn]_{unk}$$

$$A_{unk}[Mn]_{std} = [Mn]_{unk}\left(A_{unk+std} - A_{unk}\right)$$

$$[Mn]_{unk}\left(A_{unk+std} - A_{unk}\right) = [Mn]_{std} \bullet A_{unk}$$

$$[Mn]_{unk} = [Mn]_{std} \bullet \left(\frac{A_{unk}}{A_{unk+std} - A_{unk}}\right) \quad \text{Eqn1}$$

Note that equation 1 above is the concentration of the $[Mn]_{unk}$ in the cuvette (the sample that is analyzed). Dilution correction must be applied to calculate the true [Mn] concentration of the original stock solution which will lead to the % Mn in the steel.

Procedure

Preparation of a standard manganese(II) solution

If the solution has not prepared for you by the lab tech follow the directions below to prepare the standard manganese(II)sulfate monohydrate solution.

Your instructor may pair you up for the preparation of the manganese(II) standard. If this is the case, then all you need to do is prepare one Mn^{+2} solution for you and your assigned partner. You need to analyze your own sample and that means you both need to prepare solutions for your own unknown.

1. Dry 2 g of $MnSO_4 \cdot H_2O$ at 110°C for 1 h and cool in a desciccator.

2. Weigh accurately 0.30 to 0.31 g of the dried reagent, dissolve in a small volume distilled water. Transfer to a 1-L volumetric flask.

3. Dilute to the mark with distilled water, mix, and transfer to a storage bottle.

Analysis of the unknown

1. Use three identical steel samples and weight each between 0.5 and 1.0 g. Transfer each to a separate 250-mL Erlenmeyer flasks.

2. In the hood, add 50 mL of 6 M HNO_3 to dissolve the sample and boil to remove yellow-brown nitrogen oxides.

   Caution: Nitric acid is very corrosive, use safety goggles and gloves when handling this reagent. If any chemical splashes to your skin or clothing, wash immediately with copious amount of water.

3. In small portions, slowly add about 1 g of $(NH_4)_2S_2O_8$ and boil gently for 10 to 15 min. If a permanganate color develops or brown, insoluble MnO_2 begins to form, add 0.1 g of Na_2SO_3 and boil for another 5 min to decolorize the solution and remove sulfur dioxide.

   Caution: The hot solution will erupt vigorously if too much $(NH_4)_2S_2O_8$ and Na_2SO_3 are added one time.
   Small portions must be added so that the solution does not boil over.
   Stop heating the mixture when the formation of brown fumes stops evolving.

4. Cool and transfer the solutions and rinsing to numbered l00-mL volumetric flasks and dilute to the mark with distilled water. Mix well.

5. Pipet 25-mL aliquots of the first sample into three separate 125-mL beakers. To the first beaker (unknown) add 5 mL of concentrated H_3PO_4 and 0.5 g of KlO_4. To second beaker (unknown + standard) add the same amount of H_3PO_4 and KlO_4 plus 5.00 mL (pipet) of the standard manganese solution. To the third beaker (blank) only 5 mL of H_3PO_4.

6. Gently boil each solution for 5 min. When cool, transfer to numbered 50-mL volumetric flasks and dilute to the mark with distilled water.

7. Measure the absorbance of solutions 1 and 2 at 525 nm versus solution 3 as reference. Repeat steps 5 through 7 with the two remaining samples. (You should have a short narrative on the spectrometer use and the parameter settings used in the experiment.

8. Print the spectra collected, label key information on each spectrum and attach to your report in the appendix as supplement data. Add only the spectra and not superfluous information.

9. Use the standard addition equation to calculate the amount of manganese in each measured solution and then calculate the % Mn in the sample.

Calculations-

Analysis

Calculate the manganese concentration in the standard. (Note the formula of the chemical used)
Calculate the manganese concentration in steel, M
Calculate the weight percent of manganese in steel sample
Complete the data table below using your raw data

Raw Data for Volumetric Glassware:

Sample Data Table

	Sample 1			Sample 2			Sample 3		
Mass $MnSO_4 \cdot H_2O$ standard, g									
Conc. $MnSO_4 \cdot H_2O$ standard, M									
Mass steel, g									
Step 6	Beaker1	Beaker2	Blank	Beaker1	Beaker2	Blank	Beaker1	Beaker2	Blank
Vol steel solution, mL									
H_3PO_4 and KIO_4 added									
Volume standard, mL									
Water added									
Total Volume (Step 6)									
Absorbance									

Statistic Analysis –

i) Report the average, standard deviation (σ) and relative deviation (RSD, σ_r) and the coefficient of variation (CV) .
ii) Apply a Q-test to any suspected result.

Results –

Include in your summary table the items shown below -

Sample table of result summary:

Sample Result Table

	Solution 1	Solution 2	Solution 3
$[MnSO_4]_{std}$, M			
A_{unk}			
$A_{std + unk}$			
Step 6: $[MnSO_4]_{unk}$, M			
Step 4: $[Mn^{+7}]_{unk}$, M			
Step 4: Mass of $[Mn^{+7}]_{unk}$, g			
% Mn in steel, %			
Average % Mn in steel			
Standard Deviation			
RSD			
CV			

Discussion-

The goal of this experiment was to determine the percentage of manganese in steel. In general, there is less than 1% of manganese in steel. Discuss the importance of manganese in steel. What role does manganese play in the strength of steel. Is the result from your experiment consistent with the literature value. Discuss the standard deviation of the result and how the error analysis provides information to a contractor using the steel material you analyzed..

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Analytical Chemistry 251

#	**CRITERIA** (Tentative point distribution - may change depending on experiment)	pts %
1	Quiz / Homework	0
2	**Introduction and Procedures** A. Introduction • Objective of Expt. • Background information. • Math relationship used in study. B. Procedures • Outline of procedures in Expt. • Flow chart pictorial of procedures. • Procedural changes. • Information (data) to be recorded during expt. (to be presented in <u>Table form.)</u> • Safety and disposal information. **This portion of the report should be turned in before the start of lab class (prelab discussion).**	10
3	**Data, Observe., Results and Calc.** C. Data and Observation • Data in <u>table form.</u> & detailed observation written in the table. All data entry should contain the proper number of significant figures and units. Data should always be recorded in an organize fashion. • Balance chemical equations; all chemical reaction which occurred during an experiment should be written in this section. Then it should also be written in the discussion portion of the report. • A short narrative should be included about the spectrometer that was used and the settings used in the measurment. **This portion of the report should be turned in before you leave the laboratory.**	10
	Calculations & Results D. Calculations • Sample calculation shown. • Statistical analysis of data and result (if applicable) E. Results • Result(s) in <u>table form</u>. In this section accuracy of results is very important as well as detailed calculation showing how the result was obtain. "Unknown" will also be included in this section.	15 15
4	**Discussion / Conclusions and Post-Lab Questions** F. Discussion •A complete discussion should be written in this section. Topics to be discuss can be found at the end of each experimental procedure from the lab manual. Each discussion should include the significance of the result(s) and the meaning of the result of the experiment. All chemical reactions that occurred during the experiment should also be included here. G. Conclusion • Summary of the goal of the experiment and how that goal was achieved in the experiment. H. Post-lab questions from manual or class assignment • Complete well thought-out answers. **This portion (Calculation and Discussion) is turned in at the beginning of class of the due-date**	10
5	**Overall Presentation (of lab notebook)** • Lab technique during experiment; example are, class preparation, safety glasses precautions and leaving the laboratory clean. • Report presentation: examples are the headings of each report that includes name, title, lab partner, date and section #. • Legibility of report. Is the report easy to read or is important information jotted down by small print in the corners of the lab report. The overall impression is important.	10
6	Lab Technique • Safety: wear goggles, handle chemicals with caution, proper handling of lab equipment • Leave lab clean and tidy	10
	Total (This total may be adjusted depending on lab technique and student conduct in the experiment)	80 / 2

Lab Tech Notes:

Find steel samples so that students can have a variety of unknown.

Do standard additon and cabibration curve, do a student-t to compare results.