Experiment: Determination of Manganese in Steel

Manganese (Mn) in steel may be determined upon dissolution as manganese (VII) after oxidation from the manganese oxidation state (II). This procedure calls for three oxidizing agents. Manganese (VII) may be determined spectrophotometrically.

During dissolution of the sample with dilute nitric acid to form iron (II) and manganese (II), nitrogen oxide gases are formed. These must be removed, partially by boiling, and the rest with ammonium peroxydisulfate which also removes carbon or other organic matter present. The nitrogen oxides may react with periodic acid which is used to convert manganese to the (VII) oxidation state. Excess peroxydisulfate is decomposed by boiling.

The equations are:

$3\ Mn + 2\ NO_3^- + 8H^+ \ ---> 3\ Mn^{2+} + 2\ NO\ (g) + 4H_2O$

$2\ NO_2\ (g) + S_2O_8^{2-} + \ 2\ H_2O \ ---> 2\ NO_3^- \ + 2\ SO_4^{2-} \ + 4\ H^+$

$2\ S_2O_8^{2-} + \ 2\ H_2O \ + \ heat \ ---> 4\ SO_4^{2-} \ + \ O_2 + 4\ H^+$

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

$NO(colorless\ gas) + 1/2\ O_2\ (g) <---> NO_2\ (brown\ gas)$

Note: Peroxydisulfate has the required oxidizing potential to change the oxidation state of manganese from (II) to (IV), but the reaction is too slow. Silver could be employed catalytically but the results are too erratic. Periodate oxidizes the manganese to the (VII) state quantitatively and rapidly at the boiling point, and it is advisable to add the sparingly soluble periodate salt in several portions to maintain an excess and to allow for some decomposition of the latter salt at the elevated temperatures.

PROCEDURE:

Use <u>one</u> standard steel sample containing known quantities of manganese and <u>two</u> unknown samples.

NOTE: DO NOT DRY THE MANGANESE (Mn) SAMPLES IN THE OVEN.

For ease of calculation, weigh accurately 0.2 g for the standard (0.94% of Mn, you can find it on the chemical shelf) and unknown steel (to within 0.01 g of each other). Note that if the digital electronic balance is used, the sample vial being weighed should be placed on top of an inverted 50 mL beaker since the sample is ferromagnetic and thus may interfere with the balance mechanism.

Place the 3 steel samples in three separate 100 mL beakers **<u>In the fumehood</u>**, add to each beaker 10 mL 1:3 nitric acid [prepare 40 mLs total (10 mL of conc. HNO_3: 30 mL H_2O)]. Cover each solution with a watch glass; boil gently for two minutes to remove nitric oxide. The black residue which may remain is probably carbon which will not interfere if allowed to settle later in the volumetric flask.

Remove the beaker from the heating source, carefully sprinkle 0.2 g ammonium persulfate (the same as ammonium peroxysulfate) into the solution. Boil gently for 15 minutes to destroy excess persulfate and carbon.

Dilute the solution to approximately 20 mL, add 3 mL of stock 85% phosphoric acid, and 0.10 g potassium periodate. After boiling gently for several minutes to cause the oxidation to permanganate, remove the heat source, and while the solution is still hot, but not boiling, add another 0.1 g portion of g potassium periodate. You may need a further 0.04 g portion if the permanganate color does not develop. If a precipitate of small dark particles is seen at this point, add 0.10 g sodium bisulfite, heat, re-add 0.04 g of potassium periodate and reheat. If it does not respond to this treatment, it is probably carbon. After cooling, transfer quantitatively to a 100 mL volumetric flask and make up to volume. The solution may be stored in a dry, stoppered 100 mL or 250 mL Erlenmeyer flask.

Carry out a serial, quantitative dilution of one of the standard sample 4 times (each time by a factor of 2) to determine if Beer's Law is obeyed (see below). Refer to your textbook or notes for a more detailed discussion of Beer's Law. If you don't know how to perform serial dilution, you may refer your lab manual of "Determination of Copper by Anodic Stripping Voltammetry" Page 1, Line 31.

SPECTROPHOTOMETRIC DETERMINATION (refer to your textbook for appropriate theoretical discussion):

Follow the operating procedure below. Fill the reference cell with distilled water and the sample cell with one of the standard steel solutions. Take readings at 480, 520, 560, and 600 nm. Note that at every change in wavelength, the reference cell must first be used to set the absorbance to zero. Select the wavelength of peak absorbance, (λ_{max}). At $\lambda = \lambda_{max}$, measure Absorbance (A, y-axis) vs. concentration (x-axis). To do this, absorbance at λ_{max} is measured for each of the diluted standards as well as the undiluted standard and the two undiluted unknown solutions. It is convenient to express the concentration in terms of % Mn instead of using molar concentrations since the initial weights and the final volumes of the unknowns and standards are equal to each other. It takes about 2 mL of solution in the sample cell to obtain a reading. Be sure to use the same sample cell for all your calibrations and measurements. Record your results in the same table format as on the attached sheet. Since the same sample cell is used several times, it is important to rinse the sample cell quantitatively with the next unknown sample solution to be measured. Draw a plot of absorbance (A, y-axis) vs. wavelength (λ, x-axis) to determine the optimal wavelength (λ_{max}). At $\lambda=\lambda_{max}$, determine if Beer's Law is observed by plotting (see example graph attached) Absorbance (A, y-axis) vs. concentration (%Mn, x-axis). The standard (calibration) curve is obtained by drawing the best straight line that most closely approximates the data points. Use this curve to determine the % Mn corresponding to the absorbance of the unknown solutions. Both of these plots are to be included with your informal report.

It is possible to determine the %Mn of the unknown algebraically by using the Beer's Law equation and taking ratios. For example, $A_{unk} = \varepsilon c_{unk} b$ and $A_{std} = \varepsilon c_{std} b$ or, $A_{unk}/A_{std} = c_{unk}/c_{std}$.
where $c_{unk} = (\%Mn)_{unk}\ (mass)_{unk}/V_{unk}$ and $c_{std} = (\%Mn)_{std}\ (mass)_{std}/V_{std}$.
In this experiment, the volumes are equal: $V_{std} = V_{unk}$.

Or, one can, calculate the molar absorptivity, ε, of permanganate from the standard sample and apply this to the unknown sample using Beer's Law.

Because the algebraic methods of calculation outlined above presume that the data lie on the standard curve, it may be more prone to error than the graphical method using the standard curve. As such, the informal report should be based on the graphical method for greater accuracy.

NOTE:

A. Ferric ions interact with permanganate ions to reduce the absorbance of permanganate slightly. Thus, standard steel is used for correction. Should standard permanganate solution be used, ferric nitrate must be added.

B. During the addition of ammonium persulfate, black manganese oxide may form. It may be redissolved by the addition of a few drops of dilute sodium sulfite solution followed by boiling to expel sulfur dioxide.

C. Complexes of ferric ion with phosphoric acid do not absorb visible light while ferric ion in nitric or hydrochloric acid absorbs appreciably at 520 nm.

D. Analyze permanganate solutions on the day of preparation or add excess periodate and store in a sealed vessel in the dark. Periodate prevents permanganate from slow reduction.

FURTHER READING:

1. A. I. Vogel, "Textbook of Quantitative Inorganic Analysis", Longman, London (1961).

2. G. D. Christian, "Analytical Chemistry", John Wiley and Sons, New York (1977).

*Operating procedures for the spectrophotometer:
Turn on the spectrophotometer using the on/off switch at the back of the device and let it warm up for about 10 minutes. Have 2 identical cuvettes – one a reference cell (to be filled with the "blank" solution, which in this case is water), and the other a sample cell (to be filled with the absorbing solutions). Have all your solutions (the 2 undiluted unknown solutions, the standard - both undiluted and diluted) ready when measurements are made. It is important to make all the measurements in a single sitting to minimize drift in the data. It is necessary to "zero" the absorbance first whenever the wavelength is changed. To zero the absorbance, set the wavelength by scrolling the wavelength up or down using the "nm" or "nm" buttons. Insert the reference cell (with the blank solution) into the cuvette holder making sure it is properly aligned to maximize the pathlength through the solution. Close the cover and press the "O Abs" button and wait for the digital read out to adjust to zero. The sample cell can now be inserted in place of the reference cell. The digital readout is the absorbance data for the sample solution.

Note: Discard all waste in appropriate bottles as instructed. If you have any questions, please see your instructor or teaching assistant before disposing of waste.

Informal report: Date submitted: _____
Experiment: Determination of Manganese (Mn) in Steel Time submitted: _____

Name: _____ Values obtained:

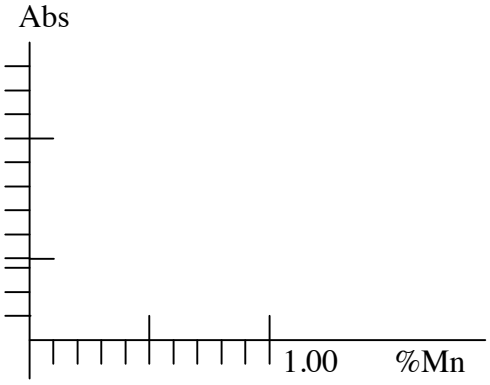
(1) _____ %

Locker #_____ (2) _____ %

Average value = _____ %

Data for calibration curve

Solution (expressed as % Mn)	Absorbance
.058	
.118	
.235	
.47	
.94 (undiluted standard)	
unknown #1	
unknown #2	



Note: Draw the calibration curve in your laboratory notebook and attach a copy with your lab report as you turn it in to be graded.