

(Modified experiment from CHEM 325, FALL 2008)

05

SPECTROPHOTOMETRIC DETERMINATION OF MANGANESE IN STEEL

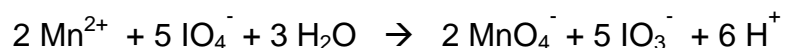
Purpose:

To use previously acquired skills in analysis of a real-world sample

Materials:

spectrometer, cuvettes
steel sample unknowns
nitric acid
phosphoric acid
potassium permanganate
potassium periodate
ammonium peroxodisulfate
ammonium (or sodium) hydrogen sulfite
pipettes, volumetric flasks, labels, beakers

Small quantities of manganese are readily determined colorimetrically by oxidation of its soluble salts to the highly colored permanganate ion. Potassium periodate is effective oxidizing agent for this purpose.



Acidic permanganate solutions containing excess of periodate are relatively stable.

Interferences to this procedure are few. The presence of colored ions can be compensated by employing as a blank an aliquot of the sample that has not been oxidized by periodate. This method of correction is not effective in the presence of appreciable quantities of cerium(III) or chromium(III), because both are oxidized by the periodate to a greater or lesser extent and their oxidative products absorb in the region commonly employed for the permanganate.

The following method is applicable to most steels except to those containing large amounts of chromium. Alternative method (Laboratory experiment 05(b)) allows simultaneous determination of manganese and chromium in steel. Your unknown sample will not contain appreciable amounts of chromium.

The solid sample (steel filings) is dissolved in nitric acid. Any carbon residue present is removed by oxidation with peroxodisulfate. Phosphoric acid is added to complex the iron(III) and to prevent the color of uncomplexed iron(III) species from interfering with the analysis. One aliquot of each sample is carried

through the entire procedure, except that no periodate is added, to serve as a blank and correct for the presence of colored foreign ions.

Procedure: A spectrophotometer (Spectronic 20M) set at 525 nm will be used for absorbance measurements. After allowing the instrument to warm up, set the 0 % and 100 % transmittance. (Consult the manual or follow TA instructions for instrument operation.)

1. Preparation of standard KMnO_4 solutions. Prepare a solution that contains the equivalent of 0.10 g Mn per liter. This may be accomplished by dilution of a previously standardized solution of KMnO_4 . (Note: a 0.10 N KMnO_4 solution contains 1.09876 g Mn/liter).

Transfer 5.00 ml of the standard permanganate solution to a 50-ml volumetric flask and dilute to the mark. Rinse and fill one of the absorption cells of the instrument with this solution; fill a second cell with water and dry the walls of both with a clean tissue. Determine the absorbance of the solution. Prepare a series of standards (at least 3 more) in the same way to cover an absorbance range between 0.1 and 1.0. Plot a calibration curve.

2. Analysis of steel. Weigh triplicate 0.8-g samples of the steel and dissolve each in 50 ml of 4 mol/l HNO_3 while boiling. Heating for 5 minutes should suffice. Cautiously add about 1 g of solid ammonium peroxodisulfate and boil gently for 10-15 minutes. If the solution is pink or contains brown oxide of manganese, add approximately 0.1 g of sodium hydrogen sulfite or ammonium hydrogen sulfite and heat for another 5 minutes. Cool and dilute the solutions to exactly 100 ml in volumetric flasks.

Pipette two 25 ml aliquots of each sample into small beakers and add 3 to 5 ml of concentrated H_3PO_4 .

Again, add 0.4 g of KIO_4 to one of the two aliquots and boil for 5 minutes; the untreated serves as the blank. Cool first and then dilute both aliquots to exactly 50 ml in volumetric flasks. Determine the absorbance of the periodate-treated sample against the blank, and calculate the milligrams of manganese from the calibration curve. If necessary, perform additional dilutions of your sample to bring the observed absorbance within the 0.1 - 1.0 absorbance range. Make sure to record all dilutions. Repeat this procedure for each of the three samples.

Calculate the percent manganese (and standard deviation) in the steel sample.

3. Calibration using low absorbance method. This technique is useful for improving the accuracy of absorbance methods when the concentration of the absorbing species is low and/or when a low absorbing blank is employed. Generally, if the concentration of absorbing species in the sample or blank is so low that transmittance measured in the standard procedure lies in the range of 80 % ($A = 0.1$ or less), the low absorbance method can be used to improve the accuracy of the analytical measurement. In this method, a standard solution that

is somewhat more concentrated than the sample is employed to adjust the zero reading of the indicator scale; the 100 % transmittance is set using DI water as above. The relative transmittance of the sample (and blank) is then determined in the usual way.

Repeat the absorbance measurements of your blanks and samples, and calculate the percent manganese in your steel sample using the low absorbance method.

Report results (% Mn + s.d.) obtained from both the conventional and the low absorbance method.

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