25. Measuring Manganese in Steel by Spectrophotometry with Standard Addition

Green Profile
See Section 0

Experiments 24–26 illustrate a sequence in which students (1) prepare and standardize a Mn^{2+} solution and then (2) use this standard in the analysis of Mn in steel by two different instrumental techniques.[41] In this experiment, steel is dissolved in acid and its Mn is oxidized to the violet colored permanganate ion, whose absorbance is measured with a spectrophotometer:

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

$2Mn^{2+}$	$5IO_4^-$	$3H_2O$	$2MnO_4^-$	$5IO_3^-$	$6H^+$
(colorless)	Periodate (colorless)		Permanganate (violet) $\lambda_{max} \approx 525$ nm	Iodate (colorless)	

Steel is an alloy of iron that typically contains ~0.5 wt% Mn plus numerous other elements. When steel is dissolved in hot nitric acid, the iron is converted to Fe(III). Spectrophotometric interference in the measurement of MnO_4^- by Fe(III) is minimized by adding H_3PO_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. Appreciable Cr in the steel will interfere with the present procedure. Carbon from the steel is eliminated by oxidation with peroxydisulfate ($S_2O_8^{2-}$):

$$C(s) + 2S_2O_8^{2-} + 2H_2O \rightarrow CO_2(g) + 4SO_4^{2-} + 4H^+$$

Reagents

3 M Nitric acid: (150 mL/student) Dilute 190 mL of 70 wt% HNO_3 to 1 L with water.

0.05 M Nitric acid: (300 mL/student) Dilute 3.2 mL of 70 wt% HNO_3 to 1 L with water.

Ammonium hydrogen sulfite: (0.5 mL/student) 45 wt% NH_4HSO_3 in water.

Potassium periodate (KIO_4): 1.5 g/student.

Unknowns: Steel, ~2 g/student. Analyzed samples are available from Thorn Smith.[2]

Procedure

1. Steel can be used as received or, if it appears to be coated with oil or grease, it should be rinsed with acetone and dried at 110°C for 5 min, and cooled in a desiccator.
2. Weigh duplicate samples of steel to the nearest 0.1 mg into 250 mL beakers. The mass of steel should be chosen to contain ~2-4 mg of Mn. For example, if the steel contains 0.5 wt% Mn, a 0.6-g sample will contain 3 mg of Mn. Your instructor should give you guidance on how much steel to use.
3. Dissolve each steel sample separately in 50 mL of 3 M HNO_3 by gently boiling in the hood, while covered with a watchglass. If undissolved particles remain, stop boiling after 1 h. Replace the HNO_3 as it evaporates.
4. *Standard Mn^{2+} (~0.1 mg Mn/mL):* While the steel is dissolving, pipet 10.00 mL of standard Mn^{2+} (~1 mg Mn/mL) from Experiment 24 into a 100-mL volumetric flask, dilute to the mark with water, and mix well. You will use this solution in Experiments 25 and 26. Keep it stoppered, and wrap the stopper with Parafilm or tape to minimize evaporation.
5. Cool the beakers from step 3 for 5 min. Then carefully add ~1.0 g of $(NH_4)_2S_2O_8$ or $K_2S_2O_8$ and boil for 15 min to oxidize carbon to CO_2.
6. If traces of pink color (MnO_4^-) or brown precipitate (MnO_2) are observed, add 6 drops of 45 wt% NH_4HSO_3 and boil for 5 min to reduce all manganese to Mn(II):

$$2MnO_4^- + 5HSO_3^- + H^+ \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$$
$$MnO_2(s) + HSO_3^- + H^+ \rightarrow Mn^{2+} + SO_4^{2-} + H_2O$$

   (The purpose of removing colored species at this time is that the solution from step 6 is eventually going to serve as a colorimetric reagent blank.)
7. After cooling the solutions to near room temperature, filter each solution quantitatively through #41 filter paper into a 250-mL volumetric flask. (If gelatinous precipitate is present, use #42 filter paper.) To complete a "quantitative" transfer, wash the beaker many times with small volumes of hot 0.05 M HNO_3 and pass the washings through the filter to wash liquid from the precipitate into the volumetric flask. Finally, allow the volumetric flasks to cool to room temperature, dilute to the mark with water, and mix well.
8. Transfer ~100 mL of solution from each 250-mL volumetric flask to clean, dry Erlenmeyer flasks and stopper the flasks tightly. Label these solutions A and B and save them for atomic

absorption analysis in Experiment 26. To help prevent evaporation, it is a good idea to seal around the stoppers with a few layers of Parafilm or tape.

9. Carry out the following spectrophotometric analysis with one of the unknown steel solutions prepared in step 7:

   a. Pipet 25.00 mL of liquid from the 250-mL volumetric flask in step 7 into each of three clean, dry 100-mL beakers designated "blank," "unknown," and "standard addition." Add 5 mL of 85 wt% H_3PO_4 (from a graduated cylinder) into each beaker. Then add standard Mn^{2+} (0.1 mg/mL from step 4, delivered by pipet) and solid KIO_4 as follows:

Beaker	Volume of Mn^{2+} (mL)	Mass of KIO_4 (g)
Blank	0	0
Unknown	0	0.4
Standard addition	5.00	0.4

   b. Boil the unknown and standard addition beakers gently for 5 min to oxidize Mn^{2+} to MnO_4^-. Continue boiling, if necessary, until the KIO_4 dissolves.

   c. Quantitatively transfer the contents of each of the three beakers into 50-mL volumetric flasks. Wash each beaker many times with small portions of water and transfer the water to the corresponding volumetric flask. Dilute each flask to the mark with water and mix well.

   d. Fill one 1.000-cm-pathlength cuvet with unknown solution and another cuvet with blank solution. It is always a good idea to rinse the cuvet a few times with small quantities of the solution to be measured and discard the rinses.

   e. Measure the absorbance of the unknown at 525 nm with blank solution in the reference cuvet. For best results, measure the absorbance at several wavelengths to locate the maximum absorbance. Use this wavelength for subsequent measurements.

   f. Measure the absorbance of the standard addition with the blank solution in the reference cuvet. The absorbance of the standard addition will be ~0.45 absorbance units greater than the absorbance of the unknown (based on adding ~0.50 mg of standard Mn^{2+} to the unknown).

10. Repeat step 9 with the other unknown steel solution from step 7.

Data Analysis

1. From the known concentration of the Mn standard in step 4, calculate the concentration of added Mn in the 50-mL volumetric flask containing the standard addition.
2. All of the Mn^{2+} is converted to MnO_4^- in step 9. From the difference between the absorbance of the standard addition and the unknown, calculate the molar absorptivity of MnO_4^-. Compute the average molar absorptivity from steps 9 and 10.
3. From the absorbance of each unknown and the average molar absorptivity of MnO_4^-, calculate the concentration of MnO_4^- in each 50-mL unknown solution.
4. Calculate the weight percent of Mn in each unknown steel sample and the percent relative range of your results:

$$\% \text{ relative range} = \frac{100 \times [\text{wt\% in steel 1} - \text{wt\% in steel 2}]}{\text{mean wt\%}}$$