

LAB 5: Determination of Manganese in Steel

10/4/23

PURPOSE

The purpose is to find the % of Mn in the unknown using the UV-Vis array Spec. thus teaching us instrumentation and plotting wavelength.

Sn

Lab 5 - Determination of Manganese in Steel

-Determination of Manganese in Steel: Procedure posted on blackboard (37 N3)

Notes: Use the sample labeled "Steel Unk". Split the sample into three roughly equal parts, accurately weighed and recorded. Dissolve all three of these at the same time according to the instructions in the text. These are stable. A standard manganese solution is already prepared and can be obtained from the stockroom. Record the concentration of the standard Mn solution.

The next step is to prepare a set of six diluted solutions from one of your dissolved samples. Do not do this until you are assured that you can use the UV-Vis, diode array spectrophotometer today. The six standard addition solutions will contain 0.00, 1.00, 2.00, 3.00, 4.00 and 5.00 mL of the standard Mn solution. They will also contain the other reagents as described in the Table in the text. Finally, each solution must contain a constant volume of your dissolved sample. Calculate this volume based on the approximate percent of Mn in your unknown and the concentration of Mn in the standard. The volume should contain about the same amount of Mn as in 1-2 mL of the standard. Each of these six solutions is then heated to oxidize the manganese and diluted to a constant volume in, e.g. 50.0 mL in volumetric flasks. A blank is also prepared as described in the Table in the text.

Measure and record the visible spectra of the six solutions and the absorbance values at several wavelengths with absorbance maxima.

For the calculations, plot the absorbance of the solutions (at each of two wavelengths) vs. the amount of Mn added to each solution. Use regression analysis for the method of standard additions, as described in the text and in: Bruce, G. R.; Gill, P. S. J. Chem. Educ. 1999, 76, 805-807, to determine the concentration of Mn in the solution to which no standard Mn has been added, and also the uncertainty and precision. From these results calculate the mass percent of Mn in the original sample along with the uncertainty and precision for your analysis of the original sample.

37N-3 The Determination of Manganese in Steel

Discussion

Small quantities of manganese are readily determined photometrically by the oxidation of Mn(II) to the intensely colored permanganate ion. Potassium periodate is an effective oxidizing reagent for this purpose. The reaction is



Permanganate solutions that contain an excess of periodate are quite stable.

There are few interferences to the method. The presence of most colored ions can be compensated for with a blank. Cerium(III) and chromium(III) are exceptions; these yield oxidation products with periodate that absorb to some extent at the wavelength used for the measurement of permanganate.

The method given here is applicable to steels that do not contain large amounts of chromium. The sample is dissolved in nitric acid. Any carbon in the steel is oxidized with peroxodisulfate. Iron(III) is eliminated as a source of interference by complexation with phosphoric acid. The standard-addition method (see Section 8C-3) is used to establish the relationship between absorbance and amount of manganese in the sample.

A spectrophotometer set at 525 nm or a photometer with a green filter can be used for the absorbance measurements.

PREPARATION OF SOLUTIONS

Standard manganese(II) solution (sufficient for several hundred analyses). Weigh 0.1 g (to the nearest 0.1 mg) of manganese into a 50-ml. beaker, and dissolve in about 10 mL of 6 M HNO₃ (use the hood). Boil gently to eliminate oxides of

BB notes

	1	2	3	4	5	6	7	
5ml								$\rightarrow \text{H}_3\text{PO}_4$
Ø 0.4g								$\rightarrow \text{KIO}_4$
Ø Ø 1 2 3 4 5								$\rightarrow \text{Mn}_{3+2}$
# ml								$\rightarrow \text{unk}$

spot check

nitrogen. Cool; then transfer the solution quantitatively to a 1-L. volumetric flask. Dilute to the mark with water, and mix thoroughly. The manganese in 1 mL of the standard solution, after being converted to permanganate, causes a volume of 50 mL to increase in absorbance by about 0.09.

PROCEDURE

The unknown does not require drying. If there is evidence of oil, rinse the sample with acetone and dry briefly. Weigh (to the nearest 0.1 mg) duplicate samples (Note 1) into 150-mL beakers. Add about 50 mL of 6 M HNO₃ and boil gently (*use the hood*); heating for 5 to 10 min should suffice. Cautiously add about 1 g of ammonium peroxydisulfate, and boil gently for an additional 10 to 15 min. If the solution is pink or has a deposit of MnO₂, add 1 mL of NH₄HSO₃ (or 0.1 g of NaHSO₃) and heat for 5 min. Cool, transfer quantitatively (Note 2) to 250.0-mL volumetric flasks. Dilute to the mark with water, and mix well. Use a 20.00-mL pipet to transfer three aliquots of each sample to individual beakers. Treat as follows:

Aliquot	Volume of 85% H ₃ PO ₄ , mL	Volume of Standard Mn, mL	Mass of KIO ₄ , g
1	5	0.00	0.4
2	5	5.00 (Note 3)	0.4
3	5	0.00	0.0

Boil each solution gently for 5 min, cool, and transfer it quantitatively to a 50-mL volumetric flask. Mix well. Measure the absorbance of aliquots 1 and 2 using aliquot 3 as the blank (Note 4).

Report the percentage of manganese in the unknown.

Notes

1. The sample size depends on the manganese content of the unknown; consult with the instructor.
2. If there is evidence of turbidity, filter the solutions as they are transferred to the volumetric flasks.
3. The volume of the standard addition may be dictated by the absorbance of the sample. It is useful to obtain a rough estimate by generating permanganate in about 20 mL of sample, diluting to about 50 mL, and measuring the absorbance.
4. A single blank can be used for all measurements, provided that the samples weigh within 50 mg of one another.

PROCEDURE NOTES

* NO drying

* 3 beakers; UNKNOWN, dilute, and 50 mL MnO₂; add
1 g ammonium

Mn in steel: 95T71 1/1 wt calc sample size

20 mL = ±0.03

→ fill w/ DI Water
if (10)

→ add NH₄HSO₃

anyway

→ table 6M

$$\% \text{ Mn} = \left(C_x \left(\frac{\text{mol}}{\text{L}} \right) \cdot \text{aliquot} \times g \frac{\text{Mn}}{\text{mol}} \right) \times 100$$

g of unk

$$\% \text{ Mn} = \left(\frac{(0.000522 \text{ M}) \times (0.25) \times (54.938)}{0.4681 \text{ g}} \right) \times 100 = 1.53139\%$$

ERROR PROP! balance = ± 0.0002

250 mL value = ± 0.12

20 mL pip = ± 0.03

$$\frac{e_{Cx}}{C_x} = \sqrt{\left(\frac{\text{M.W.}}{\text{std. exptl error}} \right)^2 + \left(\frac{\text{b.w.}}{\text{std. exptl error}} \right)^2 + \left(\frac{\text{aliquot}}{\text{me}} \right)^2}$$

$$\frac{e_{Cx}}{C_x} = \sqrt{\left(\frac{0.00363}{0.0648} \right)^2 + \left(\frac{0.00889}{0.37163} \right)^2 + \left(\frac{0.03}{20} \right)^2}$$

$$\frac{e_{Cx}}{C_x} = 0.060946 \leftarrow \text{relative error} \xrightarrow{\text{unt}} \therefore \pm 0.06$$

Absolute ~~error~~^{unc}:

$$\cancel{e_{Cx}} = e_{Cx} = \left(\frac{e_{Cx}}{C_x} \right) \times (C_x) = 3.181 \times 10^{-5} \\ = \pm 0.0003 \text{ M}$$

% Mn error prop

Relative unc:

$$\sqrt{\left(\frac{0.0002}{0.4681}\right)^2 + \left(\frac{0.12}{250}\right)^2}$$

$$\text{Relative unc} = \sqrt{\left(\frac{0.0002}{0.4681}\right)^2 + \left(\frac{0.12}{250}\right)^2} \Rightarrow 0.000642 \\ \pm 0.0006\%$$

$$\text{Absolute unc} = (\text{Relative}) \times (\text{Mn}\%)$$

$$= (0.0006 \times 1.5313416\%) = 0.000984 \\ = 0.001\%$$

CONCLUSION

UNK # = 9ST71 Mn in steel.

~~L_x~~ FOR UNKNOWN 9ST71 the L_x was 0.0005M, this had a relative unc of $\pm 0.06\%$ and an absolute unc of ± 0.00003

The % Mn was calculated to be 1.531% with a relative unc of $\pm 0.0006\%$ and an absolute unc of $\pm 0.001\%$.

DATA

$$\text{total Mn Steel} \quad 1.4046 \quad \% = 0.4682$$

B gram

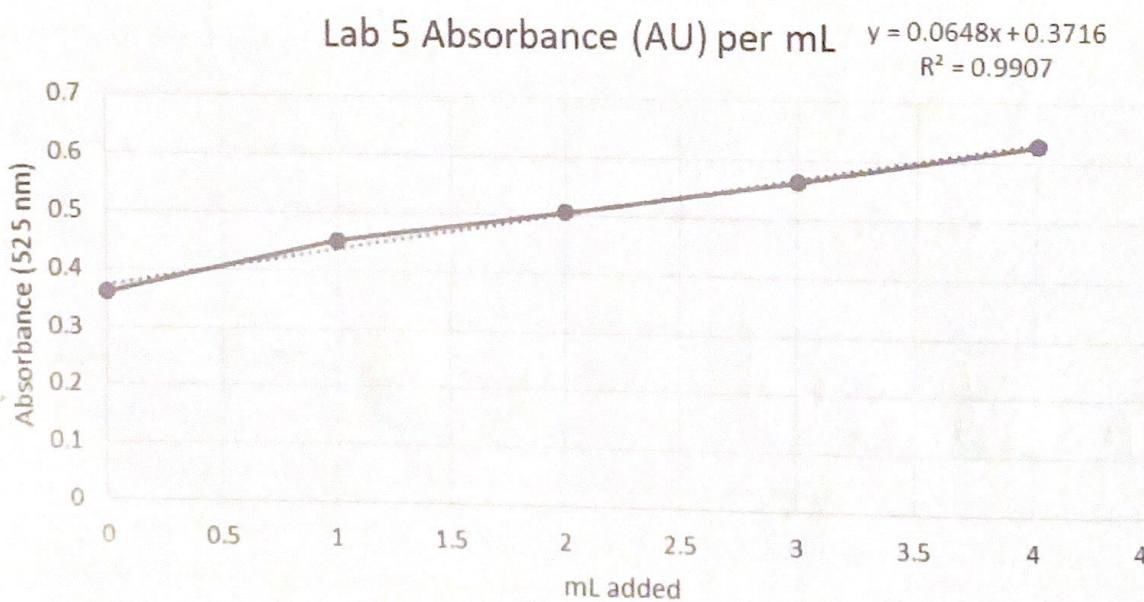
1 0.4674

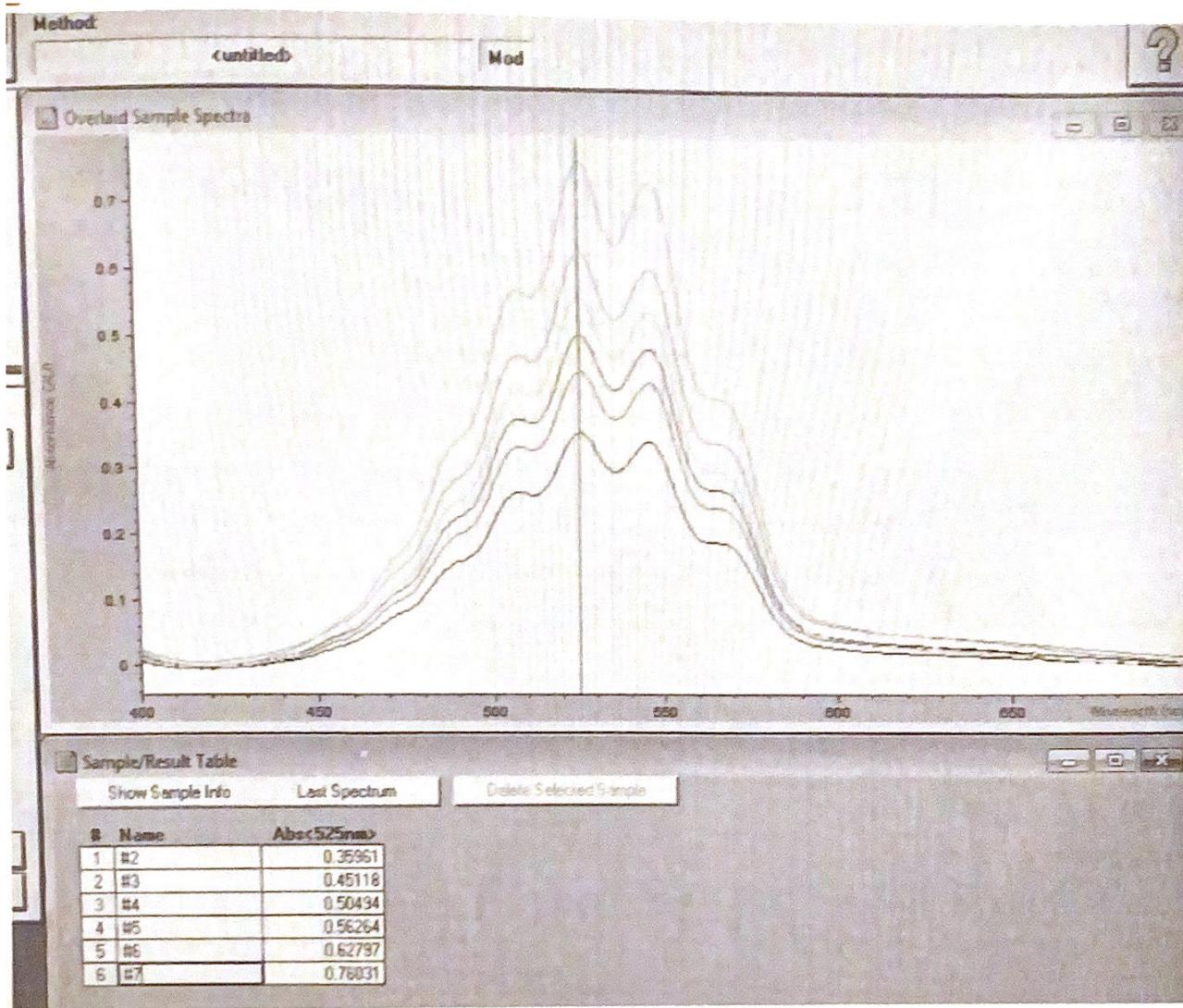
* 2 0.4681 } ← PICKED THIS ONE

3 0.4684

0.4 per g of 7 trials ± 0.02 gram KIO₄

1	Ø	Ø
2	0.4027	0.4003
3	0.4030	0.4003
4	0.4013	0.4013
5	0.4020	0.4007
6	0.4026	0.4015
7	0.4022	0.4011





HANO (ALL)

$$C_j = \text{conc of Mn in std} = (\text{Mn std}) \times \left(\frac{\text{mol Mn}}{\text{g Mn}} \right) = M$$

$$C_s = 0.1 \text{ g/L} \times \left(\frac{1 \text{ mol}}{54.938 \text{ g}} \right) = 0.00182 \text{ M}$$

$$C_x = \text{conc of Mn in unk} \quad C_x = \frac{C_s \cdot b}{V_x \cdot m}$$

$$C_x = \frac{(0.00182 \text{ M}) \cdot (0.3716)}{(20 \text{ mL}) \cdot (0.0648)}$$

$$C_x = 0.000522 \text{ M}$$