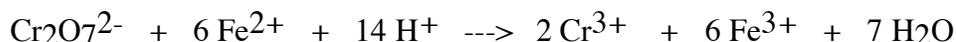


**Experiment: Determination of Iron in a Ferrous Ammonium Sulfate Sample (Fe)**

This experiment involves the determination of the percentage of ferrous iron in an unknown sample by redox titration with potassium dichromate solution as the standard using:

- (i) ferroin indicator
- (ii) potentiometric titration.

The net ionic balanced equation for the titration is:

**PROCEDURE:**

**DO NOT DRY THE (Fe) SAMPLE IN THE OVEN**

**DO NOT DRY THE POTASSIUM DICHROMATE (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) IN THE OVEN**

**Prepare the primary standard:**

Use reagent grade potassium dichromate, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> as the primary standard. Weigh accurately 1.50 g of the primary standard into a 250 mL volumetric flask and dilute to volume with distilled water.

**Prepare the unknown:**

The preparation of the unknown solution is as follows: Weigh accurately (by difference) a 5 g portion of **UNDRIED** ferrous sample into about 50 mL 1:1 sulfuric acid solution (i.e. prepared with 25 mL concentrated sulfuric acid added slowly to 25 mL distilled water with rapid stirring; solution temperature will reach 80°C) in a 250 mL beaker with vigorous stirring. Cool to a warm temperature, transfer quantitatively to a 100 mL volumetric flask, and make up to volume. Any precipitate if present will dissolve with shaking. Recheck the volume after cooling completely as the solution may shrink. If so, adjust it to the correct final volume. **ENSURE MINIMUM CONTACT OF THIS SOLUTION WITH OXYGEN.** (It is recommended that you carry out the titration soon after preparation of the unknown).

**TITRATION:**

Do three (3) indicator titrations and one (1) potentiometric titration, not necessarily in that order. For the indicator titrations, 20.0 mL aliquots of this unknown solution are titrated with the K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution using ferroin as the indicator. The color change is from red to yellow green. (The best is just as it changes color which is when it is bluish in color). If the volume of your titrant is very far from 25 mL, you may adjust the aliquots of unknown solution proportionally to make the equivalence point closer to 25 mL.

For the potentiometric titrations, use a the meter in mV mode with a platinum indicator electrode and a calomel reference electrode (set to either (+) or (-) to have it fall within the scale; if it goes below 0, switch to make it return to scale). The ferroin indicator is not needed for this titration. Allow the dichromate titrant to drain into a 150 mL beaker provided with a magnetic stirrer. To simplify obtaining a first derivative curve plot, enter the titrant by an approximate, but precisely measured volume:

For example: If the end point occurs around 15 mL, add the titrant to the following buret readings:

5.00 mL, 10.00 mL, 13.00mL, 14.00, 14.50, 14.70, 14.80, 14.90, 14.95, 15.00, 15.05, 15.10, 15.20, 15.30, 15.50, 16.00, 17.00, 20.00, 25.00 mL. (that is, Exceed the end point by about 10 mLs.)

Remember that as you add the titrant you also pay attention to the stability of the mV reading. When the change increases, make the increments small so you don't miss the actual midpoint of the equivalence point).

To determine the end point in the potentiometric titrations, plot the following curves :

- (i) E(mV) vs. volume (v in mL) of titrant,

(ii)  $\Delta E/\Delta v$  (mV/mL) vs. average  $v$  (mL).

Determine the end point from the latter (first derivative) curve. Compare the results of the two experiments.

Supplementary appendix:

### DERIVATIVES OF CURVES:

Acid-base, gravimetric, redox and complexometric titrations usually yield logarithmic curves in plots of the appropriate parameters versus volume of titrant added. (Note: pH and mV are examples of parameters which are logarithmic.). Sometimes, it is difficult to discern the endpoint of the titration, and it is useful to plot the first-derivative value versus the average volume because at the endpoint a sharp change of direction occurs. The tables below show the calculations needed to determine the first and second derivatives for raw data containing a set of mL vs mV. It is recommended that the calculations be done by computer using programs such as Excel.

Table 1: First Derivative

Point	$V_i$ (mL)	$mV_i$	$\Delta V^*$ (mL)	$\Delta mV$	$\Delta mV/\Delta V$ (mL) <sup>-1</sup>	$V_{ave}$ (mL)
1	$V_1$	$mV_1$	---	---	---	---
2	$V_2$	$mV_2$	$V_2 - V_1$	$mV_2 - mV_1$	$(mV_2 - mV_1)/(V_2 - V_1)$	$(V_2 + V_1)/2$
3	$V_3$	$mV_3$	$V_3 - V_2$	$mV_3 - mV_2$	$(mV_3 - mV_2)/(V_3 - V_2)$	$(V_3 + V_2)/2$
4	$V_4$	$mV_4$	$V_4 - V_3$	$mV_4 - mV_3$	$(mV_4 - mV_3)/(V_4 - V_3)$	$(V_4 + V_3)/2$
...						

“ \* ” = difference

A second-derivative curve of a log plot, i.e.  $\Delta^2 mV/\Delta V^2$  versus average volume,  $V_{ave}$ , yields an even more accurate plot than the first-derivative curve because a transverse line across the volume axis is obtained at the endpoint. (This is optional).

Table 2 : Second Derivative

Point	$V_i$	$mV_i$	$\Delta V^*$ (mL)	$\Delta mV/\Delta V$ (mL) <sup>-1</sup>	$\Delta^2 mV/\Delta V^2$ (mL) <sup>-2</sup>	$V_{ave}$ (mL)
1	$V_1$	$mV_1$	---	---	---	---
2	$V_2$	$mV_2$	$V_2 - V_1$	$mV'_2$ $= \frac{(mV_2 - mV_1)}{(V_2 - V_1)}$	---	$(V_2 + V_1)/2$
3	$V_3$	$mV_3$	$V_3 - V_2$	$mV'_3$	$(mV'_3 - mV'_2)/(V_3 - V_2)$	$(V_3 + V_2)/2$
4	$V_4$	$mV_4$	$V_4 - V_3$	$mV'_4$	$(mV'_4 - mV'_3)/(V_4 - V_3)$	$(V_4 + V_3)/2$
...						

“ \* ” = difference, “ ‘ ” = first derivative

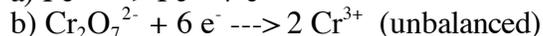
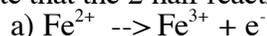
**Discarding Waste:** dichromate ( $Cr_2O_7^{2-}$ ) is toxic to the environment. After the experiment, excess  $K_2Cr_2O_7$  and the analyte are to be discarded in the designated waste bottles located on the reagent bench.

Concentrated sulfuric acid waste must be placed in the plastic, labeled acid waste container under the acid fume hood. (Alternatively, it may be neutralized with sodium bicarbonate safety solution)

Please ask the instructor or TA if you have any questions.

CALCULATING % Fe in the unknown sample:

We note that the 2 half reactions are:



Since at the equivalence point, # equivalents of  $Fe^{2+} = \#$  equivalents of  $Cr_2O_7^{2-}$ ,

we can therefore write: (#moles of Fe<sup>2+</sup>) = 6 x (# moles of Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>)

$$M_{\text{Fe}^{2+}} V_{\text{Fe}^{2+}} = 6M_{\text{Cr}_2\text{O}_7} V_{\text{Cr}_2\text{O}_7}$$

(alternatively, some write:  $N_{\text{Fe}^{2+}} V_{\text{Fe}^{2+}} = N_{\text{Cr}_2\text{O}_7} V_{\text{Cr}_2\text{O}_7}$  where N = normality = #gram equiv x molarity. In the case of a redox reactant that transfers n electrons, the normality = n x molarity).

$$\begin{aligned} \text{and: } \% \text{Fe} &= \frac{g\text{Fe} \times 100\%}{g_{\text{ore}}} = \frac{\text{molFe} (55.85\text{g/mol})}{g_{\text{ore}}} \times 100\% \\ &= \frac{6(M_{\text{Cr}_2\text{O}_7} V_{\text{Cr}_2\text{O}_7})(55.85)(100\%)}{(g_{\text{ore}})(\text{fraction titrated})} \end{aligned}$$

FURTHER READING:

1. R. B. Dean and W. J. Dixon, *Anal. Chem.*, 23, 636 (1951)
2. W. J. Dixon, *Ann. Math. Stat.*, 22, 68 (1951)
3. J. S. Fritz and G. H. Schenk, Jr., "Quantitative Analytical Chemistry" 4<sup>th</sup> Ed., Allyn and Bacon, Boston (1979)
4. L. Meites, ed., "Handbook of Analytical Chemistry". McGraw-Hill, N.Y. (1963).

**Informal report:**

Experiment: Determination of Iron

Date submitted: \_\_\_\_\_

Time submitted: \_\_\_\_\_

Name: \_\_\_\_\_

Values obtained:

(1) \_\_\_\_\_ %

Locker # \_\_\_\_\_

(indicator method) (2) \_\_\_\_\_ %

(3) \_\_\_\_\_ %

(potentiometric method) (4) \_\_\_\_\_ %

Average value = \_\_\_\_\_ %

(if applicable) Standard deviation= \_\_\_\_\_ %

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g  $K_2Cr_2O_7$  used for standard solution = \_\_\_\_\_ g

Show calculations:

$[K_2Cr_2O_7] =$  \_\_\_\_\_ M

Titration of unknown Fe ore:

g Fe ore (unknown) = \_\_\_\_\_ g

Titration:

(Ferroin indicator method)

(Potentiometric method)

I

II

III

IV

mLs of titrant  
added to reach  
end point:

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

% Fe in ore = %Fe

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

Sample calculation:

N.b. At equivalence point, milliequivalents, mEq of titrant, A = mEq analyte, B

$mEq Fe^{2+} = mEq Cr_2O_7^{2-}$ ; #mols Fe = 6 x (#mols  $Cr_2O_7^{2-}$ );

$(g Fe)/(AW of Fe) = 6(M_{Cr2O7} V_{Cr2O7}) \Rightarrow (g Fe) = 6(M_{Cr2O7} V_{Cr2O7})(AW of Fe)$

$\% Fe = (6 M_{Cr2O7} V_{Cr2O7}) (AW of Fe) (100\%) / \{(g ore) (fraction titrated)\}$

FW of  $K_2Cr_2O_7 = 294.22$  g/mol, AW of Fe = 55.85 g/mol