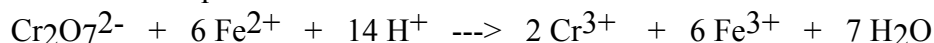


Experiment: Determination of Iron in a Ferrous Ammonium Sulfate Sample (Fe)

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 (K₂Cr₂O₇) IN THE OVEN**

Use reagent grade potassium dichromate, K₂Cr₂O₇ as the primary standard. Weigh accurately 0.75 g of the primary standard into a 250 mL volumetric flask and dilute to volume with distilled water.

The preparation of the unknown solution is as follows: Weigh accurately (by difference) a 2.5 g portion of UNDRIED ferrous sample into about 30 mL 1:1 sulfuric acid solution (15 mL conc. acid added slowly to 15 mL water with rapid stirring; solution temperature will reach 80°C) in a 250 mL beaker with vigorous stirring (Operate in hood!). Cool, transfer quantitatively to a 100 mL volumetric flask, and make up to volume. Any precipitate if present will dissolve with shaking. ENSURE MINIMUM CONTACT OF THIS SOLUTION WITH OXYGEN.

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 K₂Cr₂O₇ solution using ferroin as the indicator. The color change is from red to yellow green (best is bluish in color). Do a blank titration first in order to determine the color change. If the volume of your titrant is very far from 15 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 pH 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:

e.g. If the end point occurs around 15 mL, add the following mL increments:

5, . . . 5, . . . 2, . . . 1, . . . 1, . . . 0.5, . . . 0.2, . . . 0.1, . . . 0.1, . . . 0.05, . . . 0.05, . . . 0.05, . . . 0.05, . . . 0.1, . . . 0.1, . . . 0.2, . . . 0.5, . . . 1, . . . 1, . . . 2, . . . 5, . . . Exceed the end point by about 10 mLs.

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.

Discarding Waste: dichromate ($\text{Cr}_2\text{O}_7^{2-}$) is toxic to the environment. After the experiment, excess $\text{K}_2\text{Cr}_2\text{O}_7$ 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 container under the acid fume hood. Please ask the instructor or TA if you have any questions.

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 v (mL) vs mV (note: v and mV are your recorded data). It is recommended that the calculations be done by computer using programs such as Excel.

Table 1: First Derivative

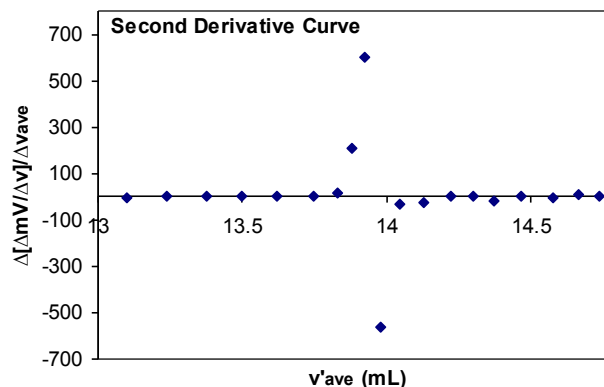
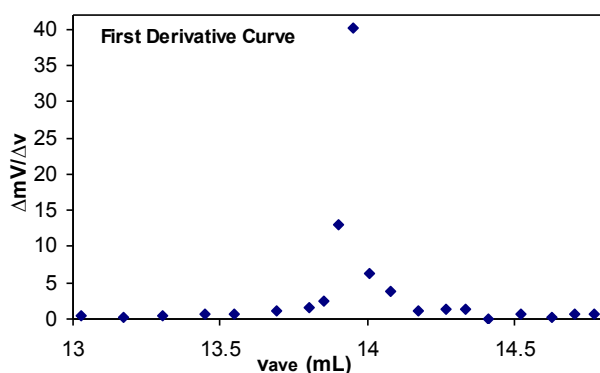
Point	v (mL)	mV	Δv (mL)	ΔmV	1 st Derivative Data	
					$\Delta mV/\Delta v$ (mL) ⁻¹	v_{ave} (mL)
1	v_1	mV_1	---	---	---	---
2	v_2	mV_2	$v_2 - v_1$	$mV_2 - mV_1$	$(mV_2 - mV_1)/(v_2 - v_1)$	$(v_2 + v_1)/2$
3	v_3	mV_3	$v_3 - v_2$	$mV_3 - mV_2$	$(mV_3 - mV_2)/(v_3 - v_2)$	$(v_3 + v_2)/2$
4	v_4	mV_4	$v_4 - v_3$	$mV_4 - mV_3$	$(mV_4 - mV_3)/(v_4 - v_3)$	$(v_4 + v_3)/2$
...						

Plot $\Delta mV/\Delta v$ (y axis) versus average volume, v_{ave} (x-axis) will give you a first-derivative curve. A second-derivative curve of, i.e. $\Delta[\Delta mV/\Delta v]/\Delta v_{ave}$ 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.

Table 2: Second Derivative

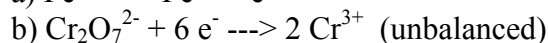
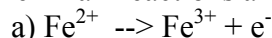
Point	1 st Derivative Data		Δv_{ave} (mL)	$\Delta[\Delta mV/\Delta v]$ (mL) ⁻²	2nd Derivative Data	
	$\Delta mV/\Delta v$ (mL) ⁻¹	v_{ave} (mL)			$\Delta[\Delta mV/\Delta v]/\Delta v_{ave}$ (mL) ⁻²	v'_{ave} (mL)
1	---	---	---	---	---	---
2	$(mV_2 - mV_1)/(v_2 - v_1)$	$(v_2 + v_1)/2$	---	---	---	---
3	$(mV_3 - mV_2)/(v_3 - v_2)$	$(v_3 + v_2)/2$	$(v_3 + v_2)/2 - (v_2 + v_1)/2$	$(mV_3 - mV_2)/(v_3 - v_2) - (mV_2 - mV_1)/(v_2 - v_1)$	$[(mV_3 - mV_2)/(v_3 - v_2) - (mV_2 - mV_1)/(v_2 - v_1)] / [(v_3 + v_2)/2 - (v_2 + v_1)/2]$	$[(v_2 + v_1)/2 + (v_3 + v_2)/2]/2$
4	$(mV_4 - mV_3)/(v_4 - v_3)$	$(v_4 + v_3)/2$	$(v_4 + v_3)/2 - (v_3 + v_2)/2$	$(mV_4 - mV_3)/(v_4 - v_3) - (mV_3 - mV_2)/(v_3 - v_2)$	$[(mV_4 - mV_3)/(v_4 - v_3) - (mV_3 - mV_2)/(v_3 - v_2)] / [(v_4 + v_3)/2 - (v_3 + v_2)/2]$	$[(v_3 + v_2)/2 + (v_4 + v_3)/2]/2$
...						

Examples of the derivative curves:



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 $\text{Cr}_2\text{O}_7^{2-}$

We can write: (#moles of Fe^{2+}) = 6 x (# moles of $\text{Cr}_2\text{O}_7^{2-}$)

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

$$\text{and: } \% \text{Fe} = \frac{g_{\text{Fe}} \times 100\%}{g_{\text{ore}}} = \frac{\text{mol Fe} (55.85 \text{ g/mol})}{g_{\text{ore}}} \times 100\%$$

$$= \frac{6(M_{\text{Cr}_2\text{O}_7}V_{\text{Cr}_2\text{O}_7})(55.85)(\text{fraction titrated})(100\%)}{g_{\text{ore}}}$$

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" 4th 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 = _____ %

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

Titrations:

(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

 $mEq Fe^{2+} = mEq Cr_2O_7^{2-}; \#mols Fe = 6 \times (\#mols Cr_2O_7^{2-});$ $(g Fe)/(AW of Fe) = 6(M_{Cr_2O_7} V_{Cr_2O_7}) \Rightarrow (g Fe) = 6(M_{Cr_2O_7} V_{Cr_2O_7})(AW of Fe)$ $\% Fe = (6 M_{Cr_2O_7} V_{Cr_2O_7}) (AW of Fe) (fraction titrated) (100\%) / (g ore)$ MW of $K_2Cr_2O_7 = 294.22$ g/mol, AW of Fe = 55.85 g/mol