

Experiment No. 01.

Date: .....

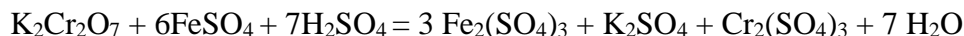
**Object:** *To determine the strength (in g/L) of ferrous ammonium sulphate ( $\text{FeSO}_4, (\text{NH}_4)_2\text{SO}_4, 6\text{H}_2\text{O}$ ) by titrating it against standard (1.0 g/L ) potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) solution.*

**Requirements:**

1. Pipette (10 ml), burette (25 ml), conical flask (100 ml), beakers
2. Ferrous ammonium sulphate [ $\text{FeSO}_4, (\text{NH}_4)_2\text{SO}_4, 6\text{H}_2\text{O}$ ] (known as Mohr's salt) solution of unknown strength
3. Standard potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) solution (1.0 g/L )
4. N-phenylanthranilic acid as indicator

**Principle:**

Ferrous ammonium sulphate [ $\text{FeSO}_4, (\text{NH}_4)_2\text{SO}_4, 6\text{H}_2\text{O}$ ] is a stable double salt with  $\text{FeSO}_4$  being its active constituent. Acidic potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) solution is a strong oxidizing agent and is rapidly reduced by ferrous ion at the ordinary temperature to a green chromic salt when added to ferrous ammonium sulphate or Mohr's salt [ $\text{FeSO}_4, (\text{NH}_4)_2\text{SO}_4, 6\text{H}_2\text{O}$ ] solution containing dilute  $\text{H}_2\text{SO}_4$ . In this reaction ferrous sulphate is oxidized to ferric sulphate, while, ammonium sulphate remains unreacted.



N-phenyl anthranilic acid is used as an indicator. Indicator is not oxidized as long as  $\text{Fe}^{2+}$  ions are there in the solution. The slight excess amount of dichromate will oxidize the indicator when all of the  $\text{Fe}^{2+}$  ions have been converted to  $\text{Fe}^{3+}$  ions resulting in colour change of the solution from greenish (due to  $\text{Cr}^{3+}$ ) to purple.

**Procedure:**

1. Burette was rinsed and filled up with potassium dichromate solution up to initial mark.
2. 10 ml of ferrous ammonium sulphate solution was pipette out and taken into a clean 100 ml conical flask.
3. 10 ml of ~5N  $\text{H}_2\text{SO}_4$  solution was added to the solution taken in the conical flask, using marked test tube.
4. Then 2-3 drops of N-phenylanthranilic acid was added into the solution as an indicator.
5. The solution mixture of flask was then titrated with constant stirring against dichromate solution taken in burette until the colour of the solution was changed from greenish to purple by a single drop addition.
6. The titration was repeated for several times until concordant burette readings were obtained.

**Observation: (on the left hand side of your laboratory note book)**

**Table:** Titration of ferrous ammonium sulphate against potassium dichromate solution (1.0 g/L).

No. of obs.	Volume of Mohr's salt solution taken ( $V_1$ mL)	Burette reading (mL)		Volume of Potassium dichromate solution required (mL)	Concordant burette reading ( $V_2$ mL)
		Initial	Final		
1	10	0.0			
2		0.0			
3		0.0			

**Calculation:**

The strength of the potassium dichromate solution =  $N_2 = 1.0 / 49.04$  (N)

Let us say the strength of ferrous ammonium sulphate solution =  $N_1$

We know  $N_1 V_1 = N_2 V_2$

Where,  $V_1$  = volume of ferrous ammonium sulphate solution taken = 10 ml

$V_2$  = volume of potassium dichromate solution required.

$$\text{Therefore, } N_1 = \frac{1.0N}{49.037} \frac{V_2}{10.0} = \left( \frac{V_2}{490.37} \right) N.$$

The strength in g/L =  $N_1 \times 392.1$  (equivalent weight of ferrous ammonium sulphate)

**Result:** The strength of ferrous ammonium sulphate solution was found to be ..... g/L.

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**Experiment no. 2:**

**Date:**

**Objective:** To determine the strength (in g/L) of the given unknown strength ferrous ammonium sulphate ( $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ ; Mohr's salt) solution using potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) solution as an intermediate solution provided with a known strength (7.8000g/L) standard Mohr's salt solution.

**Equivalent wt. of Mohr's salt: 392.14**

- Requirements:**
1. Pipette (10 ml), burette (25 ml), conical flask (100 ml), beakers
  2. Ferrous ammonium sulphate [ $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ ] solution of unknown strength and known strength.
  3. Potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) solution of unknown strength.
  4. N-phenylanthranilic acid (Fenamic) solution as indicator.

**Theory:** Ferrous ammonium sulphate ( $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ ; Mohr's salt) is stable double salt of ferrous sulphate ( $\text{FeSO}_4$ ) and ammonium sulphate ( $(\text{NH}_4)_2\text{SO}_4$ ). The active constituent of this double salt is ferrous sulphate.

Acidic  $\text{K}_2\text{Cr}_2\text{O}_7$  is a strong oxidizing agent. When it is added in the Mohr's salt solution containing dil.  $\text{H}_2\text{SO}_4$  or dil.  $\text{HCl}$ , only  $\text{FeSO}_4$  gets oxidized, while  $(\text{NH}_4)_2\text{SO}_4$  remains unchanged. The reactions take place are as follows:



where dichromate is oxidizing and ferrous salt is reducing agents. Hence, it is example of a *redox* (reduction-oxidation) reaction.

The green colour thus forms during the reaction is due to the reduced  $\text{Cr}^{3+}$  ions. Since, in this redox reaction there is no prominent colour change to indicate the end point of the titration, the addition of indicator is necessary. N-phenylanthranilic acid (Figure 1) is used as internal indicator here. Oxidized form of the indicator is of purple colour. As long as the solution contains the  $\text{Fe}^{2+}$  ions, the dichromate solution oxidizes only the  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ . When all the  $\text{Fe}^{2+}$  ions are consumed, dichromate oxidizes the N-phenylanthranilic acid and the solution become purple coloured. The colour change is sharp and hence it is easy to detect the end point.

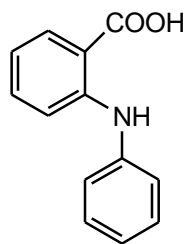


Fig. 1: N-phenylanthranilic acid

### **Procedure:**

#### **a) Standardization of $\text{K}_2\text{Cr}_2\text{O}_7$ solution with the known strength Mohr's solution:**

The burette was rinsed with potassium dichromate solution and was filled up to zero mark. 10ml of know strength Mohr's salt solution was transferred to a clean conical using a pipette. 10ml of 5N  $\text{H}_2\text{SO}_4$  and 2-3 drops indicator solution was added in that conical.

This solution was titrated by the dichromate solution until the green colour (due to  $\text{Cr}^{3+}$ ) of solution was changed sharply to light purple colour on addition of one (or max. two) drops of dichromate solution. This colour change (not the depth of the colour) indicates the end point. The titration was repeated until two concordant readings were obtained.

b) Titration with unknown strength Mohr's solution: The above procedure was repeated with the unknown strength Mohr's salt solution and the concordant readings were noted.

**Observation and Calculations:**

Weight of the Mohr's salt dissolved in distilled water: 7.8000 g/L

Normality of the solution,  $N_1 = 7.8000 / 392.14$

a) Titration with *known* strength Mohr's salt solution:

Sl. No.	Vol. of Mohr's salt solution ( $V_1$ )	Burette readings (ml)		Vol. of $\text{K}_2\text{Cr}_2\text{O}_7$ needed (ml)
		Initial	Final	
1.	10ml			
2.				
3.				
4.				

Concordant reading: .....ml ( $V_2$ )

b) Titration with *unknown* strength Mohr's salt solution:

Sl. No.	Vol. of Mohr's salt solution ( $V_3$ )	Burette readings (ml)		Vol. of $\text{K}_2\text{Cr}_2\text{O}_7$ needed (ml)
		Initial	Final	
1.	10ml			
2.				
3.				
4.				

Concordant reading: .....ml ( $V_4$ )

Since, 1 gram-equivalent wt. of Mohr's salt  $\equiv$  1 gram-equivalent wt. of  $\text{K}_2\text{Cr}_2\text{O}_7$

$$N_1 \times V_1 = N_2 \times V_2$$

$$N_2 = (7.8000 / 392.14 \times V_1) / V_2 \quad (\text{where, } N_2 \text{ is the strength of } \text{K}_2\text{Cr}_2\text{O}_7 \text{ sol.})$$

$$N_2 \times V_4 = N_3 \times V_3$$

$$N_3 = \left[ \left\{ \frac{7.8000}{392.14} \times V_1 \right\} / V_2 \right] \times V_4 / V_3$$

Hence, strength of the unknown Mohr's salt solution =  $N_3$  x eq. wt. of Mohr's salt (g/L)  
=  $\left[ \left\{ \frac{7.8000}{392.14} \times V_1 \right\} / V_2 \right] \times V_4 / V_3 \times 392.14$  g/L

Since,  $V_1 = V_3 = 10\text{ml}$

Strength of the unknown Mohr's salt solution =  $(7.8000 \times V_4) / V_2$  g/L.

**Result:** The strength of the supplied unknown strength Mohr's salt solution was .....g/L

**Note:** 1) Before the end point, colour of the solution is light green and at the end point, purple colour appears. The depth of the purple colour should not be considered, once the purple colour of the solution persists, the titration should be stooped.

2) For this titration, instead of Mohr's salt, only  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  is not used for the following reason: Ferrous sulphate salt is not stable since it gets oxidized by the oxygen (in air), when it is exposed to air. On the other hand, ferrous sulphate in Mohr's salt is quite stable.

3) The benzenoid form of N-anthranilic acid is colourless. On oxidation it gets converted to quinoid form which after dimerization forms a compound that resulted in violet-red colour solution at the end point.

4) In acid solution, the reduction of dichromate is:  $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e} \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$ , it follows that the equivalent weight is one-sixth of the molecular weight,  $294.22/6 = 49.037$  g.

**Sample questions:**

Q1. Explain the colour change that takes place at the end-point of the titration from greenish to violet-red colour.

Q2. Why only ferrous sulphate is not used to make a primary standard solution instead of ferrous ammonium sulphate?

Q3. Explain that the equivalent weight of potassium dichromate in acidic medium is one sixth of its molecular weight.

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