

## 1. CERIMETRY

PRINCIPLE:  $\text{Ce}(\text{SO}_4)_2 \cdot 2(\text{NH}_4)_2 \cdot \text{SO}_4 \cdot 2\text{H}_2\text{O}$  in  $\text{H}_2\text{SO}_4$  medium can function as a strong oxidizing agent and have a high oxidation potential. Sufficient  $\text{H}_2\text{SO}_4$  is used to prevent hydrolysis and precipitation of basic salts. Ceric Ammonium Sulphate is a salt of suitable solubility for the precipitation of the standard solution has the approximate formula  $\text{Ce}(\text{SO}_4)_2 \cdot 2(\text{NH}_4)_2 \cdot \text{SO}_4 \cdot 2\text{H}_2\text{O}$ . But the solution has to be standardized against a solution of  $\text{As}_2\text{O}_3$ . Since Ceric Ammonium Sulphate is a strong oxidizing agent we can determine various reducing substances by simple titration. In the presence of reducing agent it undergoes reduction to the cerous state for ex:



### STANDARDIZATION OF 0.1M $\text{Ce}(\text{SO}_4)_2$ :

1. Preparation of 0.1M  $\text{Ce}(\text{SO}_4)_2 \cdot 2(\text{NH}_4)_2 \cdot \text{SO}_4 \cdot 2\text{H}_2\text{O}$  : Dissolve 64gm of Ceric Ammonium Sulphate with the aid of gentle heat in a mixture of 30ml of  $\text{H}_2\text{SO}_4$  and 500ml of water. cool, filter the solution if turbid and dilute to 1000ml with water.
2. Standardization of Ceric Ammonium Sulphate : Weigh accurately about 0.2gm of  $\text{As}_2\text{O}_3$ , previously dried at  $105^\circ$  for 1 hour, and transfer to a 500ml conical flask. Wash down the inner walls of the flask with 25ml of 8% w/v NaOH solution, swirl to dissolve and add 100ml of water and mix. Add 30ml of dilute  $\text{H}_2\text{SO}_4$ , 0.15ml osmic acid, 0.1 ml ferroin sulfate solution and titration with  $\text{Ce}(\text{SO}_4)_2 \cdot 2(\text{NH}_4)_2 \cdot \text{SO}_4 \cdot 2\text{H}_2\text{O}$  solution (0.1M) until the pink color is changed to a very pale blue color.

### IP/ EQUIVALENT FACTOR:

Each ml of 0.1M  $\text{Ce}(\text{SO}_4)_2 \cdot 2(\text{NH}_4)_2 \cdot \text{SO}_4 \cdot 2\text{H}_2\text{O}$  solution = 0.004946gm of  $\text{As}_2\text{O}_3$ .

### CALCULATION:

$$\text{Molarity of } \text{Ce}(\text{SO}_4)_2 \cdot 2(\text{NH}_4)_2 \cdot \text{SO}_4 \cdot 2\text{H}_2\text{O} \text{ solution} = \frac{\text{Wt. taken} \times \text{Expected M}}{\text{Titration vol} \times \text{IP factor}}$$

### APPLICATIONS:

1. *Assay of  $\text{FeSO}_4$*  :  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , molecular weight = 278gm.

**CATEGORY:** Haematinic

**DESCRIPTION:** Bluish-green crystals or light-green crystalline powder.

**PROCEDURE:** Weigh accurately about 0.5gm of substance, dissolve in a mixture of 30ml water and 20ml 1M  $\text{H}_2\text{SO}_4$  solution and titrate with 0.1M  $\text{Ce}(\text{SO}_4)_2 \cdot 2(\text{NH}_4)_2 \cdot \text{SO}_4 \cdot 2\text{H}_2\text{O}$  using ferroin sulfate solution as indicator.

**IP FACTOR:** 1 ml of 0.1M  $\text{Ce}(\text{SO}_4)_2 \cdot 2(\text{NH}_4)_2 \cdot \text{SO}_4 \cdot 2\text{H}_2\text{O}$  = 0.01519gm of  $\text{FeSO}_4$ .

2.  $\text{FeSO}_4$  tablets
3. Dried  $\text{FeSO}_4$
4. Ferrous gluconate tablets
5. Ferrous fumarate tablets
6.  $\text{TiO}_2$
7. ascorbic acid tablets
8. Paracetamol

## 2. IODIMETRY

**DEFINITION:** Determination involving direct titration with iodine due to oxidizing powder of iodine in aqueous solution such type of titrations are called iodimetric titrations.

**PRINCIPLE:** Oxidation and reduction process involving  $I_2$  is called in general as iodimetric titrations. The direct titration with a standard solution of  $I_2$  is termed as iodimetric. Solutions of  $I_2$  are weak oxidizing agents that are used for the determination of strong oxidizing agents. The most accurate description of the half reaction for  $I_2$  in the application is :



Where  $I_3^-$  is the tri-iodide ion.

Standard  $I_2$  solutions have relatively limited applications compared with the other oxidants because of their significantly smaller electrode potential. A solution of  $I_2$  in aqueous media has an intense yellow to brown color. Since  $I_2$  solution can serve as its own indicator (self- indicator). However in practice starch solution is used as an indicator for the most accurate end point.

### STANDARDIZATION OF 0.05M $I_2$ USING $As_2O_3$ :

1. PREPARATION OF 0.05M  $I_2$  SOLUTION: Dissolve about 14gm of  $I_2$  in a solution of 36gm of KI in 100ml of water, add 3 drops of HCl and dilute with water to 100ml.

2. STANDARDIZATION OF  $I_2$  SOLUTION: Weigh accurately about 0.15gm of  $As_2O_3$  , previously dried at  $105^\circ$  for 1 hour and dissolve in 20ml of 1M NaOH by warming, if necessary. Dilute with 40ml of water, add 0.1ml of methyl orange solution and add drop wise dilute HCl until the yellow color is changed to pink. Add 2gm of  $NaHCO_3$ , dilute with 50ml of water and add 3ml of starch solution as indicator. Titrate with prepared  $I_2$  solution until permanent blue color is produced.

### IP/ EQUIVALENT FACTOR:

Each ml of 0.05M  $I_2$  solution = 0.004946gm of  $As_2O_3$ .

### CALCULATION:

$$M \text{ of } I_2 \text{ solution} = \frac{\text{wt. of } As_2O_3 \times \text{Expected M}}{\text{Titration vol} \times \text{IP Factor}}$$

### APPLICATIONS:

1. *Assay of  $Na_2S_2O_3$  (Sodium Hypo Sulphite) by iodimetry:*

Mol. wt = 248.17gm. FORMULA:  $Na_2S_2O_3 \cdot 5H_2O$

**CATEGORY:** Antidote for cyanide poisoning.

**DESCRIPTION:** large colorless crystals or coarse crystalline powder, odorless, deliquescent in moist air and effloresces in dry air , temperature above  $33^\circ$  .

**PRINCIPLE:** It is assayed by directly titrating with I<sub>2</sub> solution called as iodimetry using starch solution as indicator which is added towards the end of the titration. End point is the appearance of blue color.



**PROCEDURE:** Weigh accurately about 0.5gm of sample, dissolve in 20ml water and titrate with 0.05M I<sub>2</sub> solution using starch solution as indicator until a blue color is produced.

**IP/ EQUIVALENT FACTOR:**

Each ml of 0.05M of I<sub>2</sub> solution = 0.02482gm of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution.

**CALCULATION:**

$$\% \text{ purity} = \frac{\text{Titration vol} \times \text{IP factor} \times \text{Actual Molarity} \times 100}{\text{Wt. taken} \times \text{Expected Molarity}}$$

2. Assay of sodium meta bisulfide by iodimetry.

### 3. IODOMETRY:

**DEFINITION:** The titrations in which the equivalent amount of  $I_2$  is liberated from KI by the sample the liberated  $I_2$  is titrated against standard  $Na_2S_2O_3$  solution such a type of indirect determination of strong oxidizing agents is called iodometry.

**PRINCIPLE:** The titrations in which the liberated  $I_2$  is titrated with a standard solution of  $Na_2S_2O_3$  solution using starch-mucilage as indicator is called iodometric titrations. The indirect iodometric titration method is termed as iodometry.



#### STANDARDIZATION OF 0.1M $Na_2S_2O_3$ :

1. Preparation of 0.1M  $Na_2S_2O_3$  solution : Dissolve 25gm of  $Na_2S_2O_3$  and 0.2gm of  $Na_2CO_3$  in  $CO_2$  free water and dilute to 1000ml with water.

2. STANDARDIZATION OF  $Na_2S_2O_3$  SOLUTION: Dissolve 0.2gm of  $KBrO_3$  weighed accurately in sufficient water to produce 250ml. To 50ml of this solution add 2gm of KI and 3ml of 2M HCl solution and titrate with  $Na_2S_2O_3$  solution using starch solution as indicator until the blue color disappears.

**IP FACTOR:** Each ml of 0.1M  $Na_2S_2O_3$  solution = 0.002784gm of  $KBrO_3$ .

#### CALCULATION:

$$M \text{ of } Na_2S_2O_3 \text{ solution} = \frac{\text{Wt. of } KBrO_3 \text{ taken} \times \text{Required Molarity}}{\text{Titration vol} \times \text{IP factor}}$$

#### APPLICATIONS:

1. Assay of  $CuSO_4$
2. Bleaching powder
3. Phenol
4. Chloramine
5. Detection of chlorate
6. Determination of  $As_2O_3$
7. Determination of  $H_2O_2$
8. Determination of  $H_2SO_3$
9. Benzyl penicillin
10. Ceric sulphate

#### 1. Assay of $CuSO_4$ by iodometry:

**PRINCIPLE:** The determination of  $CuSO_4$  depends on the instability of cupric iodide formed by reaction between  $CuSO_4$  and KI in the presence of  $CH_3COOH$ .





The unstable  $\text{CuI}_2$  is decomposed to cuprous iodide and free iodine.



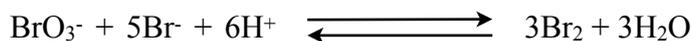
This reaction is reversible since  $\text{CuI}$  is slightly soluble, the backward reaction may be promoted. The liberated  $\text{I}_2$  can be titrated with standard  $\text{Na}_2\text{S}_2\text{O}_3$  solution using starch-mucilage solution as indicator.

**PROCEDURE:** Weigh accurately about 1gm of  $\text{CuSO}_4$  and dissolve in 50 ml of water, add 3gm of  $\text{KI}$  and 5ml  $\text{CH}_3\text{COOH}$  and titrate with liberated  $\text{I}_2$  with 0.1N  $\text{Na}_2\text{S}_2\text{O}_3$  using starch- mucilage as indicator. Continue the titration until a faint blue color remains, add 2gm of Potassium Thiocyanate. Stir well and continue the titration until the blue color disappears.

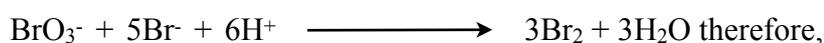
**IP FACTOR:** Each ml of 0.1N  $\text{Na}_2\text{S}_2\text{O}_3 = 0.02497\text{gm}$  of  $\text{CuSO}_4$ .

#### 4. BROMATOMETRY (Potassium-Bromate titration)

**PRINCIPLE:** Potassium Bromate is a powerful oxidizing agent which is reduced smoothly to bromide in the presence of HCl and which is then oxidized to give free bromine by bromate (excess).



The equivalent is therefore  $1/6$  moles,  $\text{KBrO}_3 / 6$  or  $167/6$  which is equal to 27.88. At the end point of titration free bromine appears.



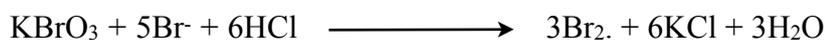
**PREPARATION OF 0.016M KBrO<sub>3</sub> SOLUTION:** Potassium bromate is usually available in a high state of purity. The analytical reagent product has an assay value of 99.9%. The substance can be dried at 120-150° is anhydrous and the aqueous solution keeps it indefinitely, it can therefore be employed as a primary standard. Its only disadvantage is that  $1/6^{\text{th}}$  of the relative molecular mass is a comparatively small quantity.

**PREPARATION:** Dissolve 2.783gm of  $\text{KBrO}_3$  in sufficient quantity of water to produce 1000ml.

#### APPLICATIONS:

1. Assay of Isoniazid
2. Determination of Hydroxylamine
3. Determination of As/Sb

**ASSAY OF ISONIAZID IP :** Anti-tubercular drug. This is determined by addition of potassium bromide and direct titration of potassium bromate in the presence of HCl solution. Bromine is released as the titration proceeds and reacts with isoniazid as shown below the Azo-dye, methyl red solution is used as an indicator which decolorises by oxidation at end point.



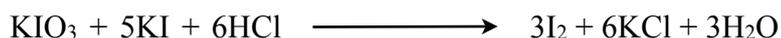
**PROCEDURE FOR ASSAY:** Weigh accurately about 0.25gm in sufficient water to produce 100ml. From this solution take 20ml and add 100ml water, 20ml HCl and 0.2gm of KBr and titrate slowly with continuous shaking with 0.016M  $\text{KBrO}_3$  solution using 0.05ml of methyl red solution as indicator until the red color disappears.

**IP FACTOR:** Each ml of 0.016M  $\text{KBrO}_3$  solution = 0.003429gm of Isoniazid ( $\text{C}_6\text{H}_7\text{N}_3\text{O}$ ).

## 5. POTASSIUM-IODATE TITRATION:

**DEFINITION:** Potassium Iodate is a powerful oxidizing agent under suitable conditions, it reacts quantitatively with both iodides and iodine, arsenides and other reducing agents. Iodate titration can be performed in presence of alcohol, saturated organic acid and many other kinds of organic matter.

**PRINCIPLE:** The reaction between potassium iodate and reducing agents such as iodide ions or  $\text{As}_2\text{O}_3$  in solutions of moderate acidity (0.12 -2M HCl) stops at the state when the iodate is reduced to iodine.



### STANDARDIZATION OF 0.05M POTASSIUM IODATE

**PREPARATION OF 0.05M  $\text{KIO}_3$  SOLUTION:** Dry some AR  $\text{KIO}_3$  at  $120^\circ$  for 1 hour and allow it to cool in a dessicator. Weigh accurately about 10.7gm of finely powdered  $\text{KIO}_3$  and dissolve in water and gently rotate the flask until the salt is completely dissolved, sufficient water is added to produce 1000ml.

**STANDARDIZATION OF  $\text{KIO}_3$  SOLUTION:** To a definite volume of  $\text{KIO}_3$  solution add excess of KI and dil.HCl and titrate the liberated  $\text{I}_2$  with  $\text{Na}_2\text{S}_2\text{O}_3$  solution.

### APPLICATIONS:

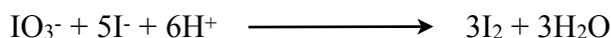
1. Potassium iodide(KI)
2. Weak  $\text{I}_2$  solution
3. Aqueous  $\text{I}_2$  solution
4. Sodium diatrizoate
5. Iodized oil fuel injection
6. Determination of Hg( $\text{HgCl}_2$ )
7. Hydralazine HCl and injection IP

### USP:

1. Benzalkonium chloride
2. Iodine tincture
3. Sodium Iodide

### ASSAY OF POTASSIUM IODATE:

**PRINCIPLE:** if the concentration of HCl is less the reaction between  $\text{KIO}_3$  and KI stops,when the iodide has been reduced to free iodine.



**PROCEDURE:** weigh accurately about 0.35gm of  $\text{KIO}_3$  dissolved in about 10ml of water, add 35ml HCl and 5ml of chloroform. Titrate with 0.05M  $\text{KIO}_3$  until the purple color of  $\text{I}_2$  disappears from the chloroform. Add the last portion of iodate solution drop wise and agitate vigorously and

continuously. Allow to stand for 5 mins, if any color develops in huge in chloroform layer continue the titration until the chloroform layer, continue the titration until the chloroform is decolorised.

**IP FACTOR:** Each ml of 0.05M  $\text{KIO}_3$  solution = 0.0166ml of KI.

## 6. DICHROMETRY(Potassium Dichromate titration)

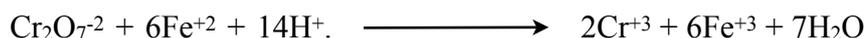
Primary standard used: Ammonium iron(II) sulphate

Indicator used: N-phenyl anthranilic acid

**PRINCIPLE:** As an oxidant, dichromate has advantages over permanganate but it is less powerful, it's use is much more limited. It is obtainable in a state of high purity and can be used as primary standard solutions of dichromate in water are state indefinite. The half reaction for dichromate is:



The most important application of dichromate is in its reaction with iron (II) in which it is often preferred to permanganate.



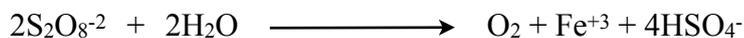
### PREPARATION AND STANDARDIZATION OF 0.1M $\text{K}_2\text{Cr}_2\text{O}_7$ :

PREPARATION OF 0.1M  $\text{K}_2\text{Cr}_2\text{O}_7$  : Weigh accurately 29.46gm of  $\text{K}_2\text{Cr}_2\text{O}_7$  and dissolve in 1000ml of water to get 0.1N solution. To prepare 1N dissolve 49.03gm of  $\text{K}_2\text{Cr}_2\text{O}_7$  in 1000ml of water.

STANDARDIZATION: To 50ml of 0.1N Ferrous Ammonium Sulphate add 20ml  $\text{H}_2\text{SO}_4$  and 1.5ml of N-phenyl anthranilic acid. Titrate the excess of iron(II) salt with  $\text{K}_2\text{Cr}_2\text{O}_7$  solution until the water changes from green to restore red color.

END POINT: Appearance of Pink/Red color.

REACTION:



### CALCULATION:

$$M_1V_1 = M_2V_2$$

$M_1$  = Molarity of  $\text{K}_2\text{Cr}_2\text{O}_7$

$V_1$  = Volume of  $\text{K}_2\text{Cr}_2\text{O}_7$  consumed (burette reading)

$M_2$  = Molarity of ammonium iron(II) sulfate

$V_2$  = Volume of ammonium iron(II) sulfate

**APPLICATIONS:**

1. Determine the % of Fe in sample of Fe wire
2. Determine ferrous and ferric ions in a solution
3. Determine ferric ion % in solution of ferric alum
4. Determine the % of Fe in Fe ore such as haematite

***DETERMINATION OF IRON USING  $K_2Cr_2O_7$ :***

**PRINCIPLE:** As an oxidant dichromate has advantages over permanganate but it is less powerful its use is much more limited. It is obtained in the state of high purity and can be used as primary standard solution of dichromate in water are stable ingredients.

The half reaction of dichromate is:



The most important application of dichromate is in its reaction with iron(II) in which it is often preferred to permanganate.

***METHOD:***

Prepare a standard dichromate solution by dissolving an accurately weighed sample of 0.4gm in water and make up the volume upto 1000ml in volumetric flask. Into the flask or beaker weigh out accurately duplicate portions about 0.7gm of iron provided (in 100ml) add 30ml of dil.  $H_2SO_4$  and 1000ml of water. 7ml of 85%  $H_3PO_4$  and 5 drops of diphenylamine sulfonate indicator. Titrate with dichromate solution and a purple color is appeared. Calculate the % of iron in solid state.