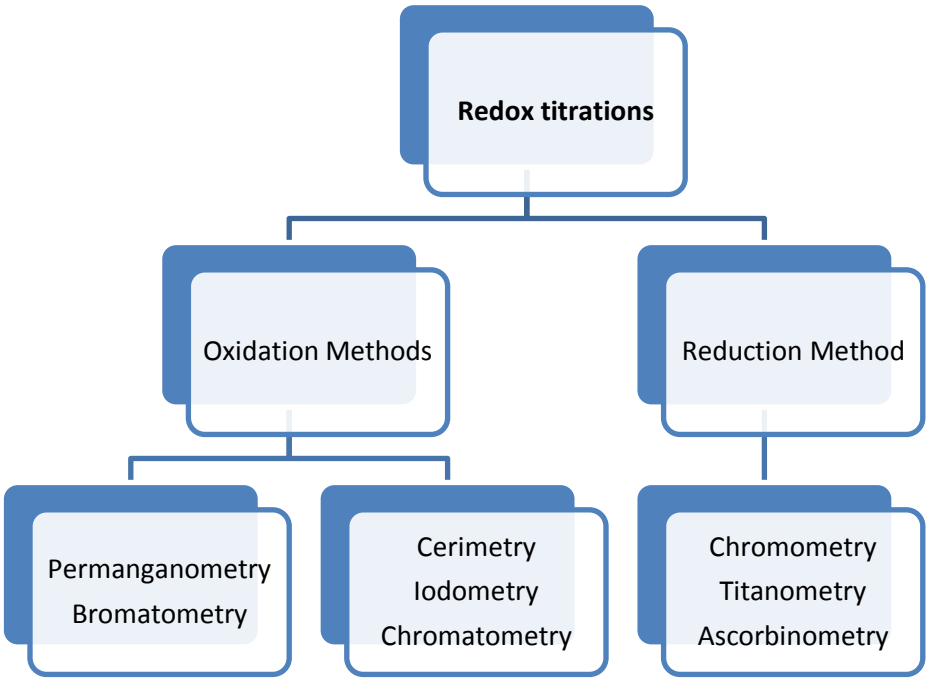
❖ Introduction

The diazotization titration is nothing but the conversion of the primary aromatic amine to a diazonium compound. This process was first discovered in 1853 and was applied to the synthetic dye industry. The reaction mechanism was first proposed by Peter Griessin. In this method, the primary aromatic amine is reacted with the sodium nitrite in acidic medium to form a diazonium salt. This method is first used in the determination of dyes.

PRINCIPLE

The principle involved in this method is that the primary aromatic amine present in the sample reacts with the sodium nitrite in the presence of acid such as hydrochloric acid to obtain a diazonium salt.

❖ Types of redox titrations



❖ **Iodometry and Iodimetry titration*:** Iodometry and Iodimetry involve oxidation-reduction reactions of Iodine. Iodine can be very conveniently titrated with standard thiosulphate solution

- **Iodimetry:** Titration in which a standard Iodine solution is used (Direct Iodometric)

$$I_2 + 2e^- \rightarrow 2I^-$$

- **Iodometry:** Titration in which Iodine liberated during chemical reaction is titrated (Indirect Iodometric)

$$2I^- - 2e^- \rightarrow I_2$$

1. Iodimetry Titration:

Principle: Iodimetry covers titration with a standard solution of iodine. Iodimetry deals with the titration of iodine liberated in chemical reaction. This method is based upon the inter conversion of elemental I_2 and iodide ion.

$$I_2 + 2e^- \rightarrow 2I^-$$

In Iodimetry, the formation if iodine takes place as a result of hydriodic acid (HI), with a oxidizing agent. The HI is obtained directly in the reaction flask by the action of dilute HCl or H_2SO_4 on a solution of KI.

$$2KI + H_2SO_4 \rightarrow K_2SO_4 + 2HI$$

Free iodine is liberated as result of the oxidation of KI in acidic solution. The iodine liberated is titrated with standard solution of sodium thiosulphate. The free iodine is converted to I^- ion (iodide ion) with reducing agent.

Thus, Iodimetry titration is used for the quantitative determination of oxidizing agent and reducing agent. Standard solution of sodium thiosulphate and iodine are used in this method with starch as indicator. With free iodine it gives blue color. Due to its greater sensitivity.

- **Conditions for Iodimetry determinations**

1. Potential of the $I2/2I^-$ system is not high.
2. Since iodine is volatile in nature, titration is conducted in the cold condition. Also, sensitivity of starch reduces with rise in temperature.
3. Iodometry titration cannot be performed in strongly alkaline solution as it forms hypoiodide.

$$2\ NaOH + I2 \rightarrow NaOI + NaI + H_2O$$

4. Since the solubility of iodine in water is low, a greater amount of KI must be used.

2. Iodometry titration

Principle: Titration in which Iodine liberated during chemical reaction is titrated (Indirect Iodometric). $2I^- - 2e^- \rightarrow I_2$

If a strong oxidizing agent ($CuSO_4$, $K_2Cr_2O_7$, $KMnO_4$) is treated in neutral or acid solution with large excess of Iodide ion , the iodide ion will act as reducing agent and the oxidant will be quantitatively reduced. The equivalent amount of Iodine will liberate, which can be then titrated using standard reducing agents. Example: If oxidant is $CuSO_4$ then

$$2Cu^{+2} + 2I^- \rightarrow 2Cu^+ + I_2 \text{ or } 2Cu^{+2} + 4I^- \rightarrow Cu_2I_2 + I_2$$

The quantity of Iodine liberated will be equivalent to concentration of Cu^{+2} or amount of $CuSO_4$

$$2CuSO_4 = 2Cu^{+2} = I_2$$

2 molecules of $CuSO_4$ will produce a molecule of Iodine, therefore if we determine the quantity of Iodine liberated that will equivalent to the amount of Cu^{+2} ions or that of $CuSO_4$

The quantity of Iodine liberated can be determined using standard thiosulphate solution

$$I_2 + Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI$$

- **Preparation of Sodium thiosulphate solution**

Sodium thiosulphate (pentahydrate) $Na_2S_2O_3$, 5 H2O is readily obtainable in a state of high purity. Because of efflorescent nature of this salt there is always uncertainty about the water content. The equivalent weight of this salt is 248.19 gm/mol.

Preparation of 0.1 M Sodium thiosulphate solution:

25 gm $Na_2S_2O_3$, 5 H2O + 0.2 gm of $Na_2Co_3 \rightarrow$ 1000 mL of distilled water

- **Titration:**

1. Titration with Potassium dichromate

Principle:

Potassium dichromate is a primary standard, it act as an oxidizing agent. In standardization of sodium thiosulphate, a known quantity of potassium dichromate is dissolved in water, acidified with hydrochloric acid; excess of potassium iodide is added. Potassium dichromate oxidizes KI to iodine and the liberated iodine is then titrated with thiosulphate using starch indicator till pale green color is occurred.

2. Titration with Potassium iodate

Principle: Potassium iodate is a primary standard. This reacts with KI in acid solution to liberate iodine. Weigh accurately pure dry potassium iodate, dissolve in cold distilled water add

potassium iodide and sulphuric acid to it titrate the liberated iodine with sodium thiosulphate with constant stirring to get pale yellow. Add starch solution and continue the titration to get colorless solution.

$$KIO_3 + 5KI + HCl \rightarrow 6KCl + 3I_2 + 3H_2O$$

Preparation of iodine 0.05 M

Iodine has less solubility in water. (0.335 g/L). Aqueous solution of Iodine has an appreciable vapor pressure of Iodine and therefore concentration of Iodine decreases due to volatilization

These difficulties can be overcome by dissolving the Iodine in an aqueous solution of KI. Iodine is readily soluble in aqueous solution of Iodide. More concentrated the solution, greater the solubility of Iodine

Dissolve about 14 gm of iodine in a solution of 36 gm of potassium iodide in 100 mL of water, add three drops of hydrochloric acid and dilute upto 1000 mL with water.

- **Detection of end point**

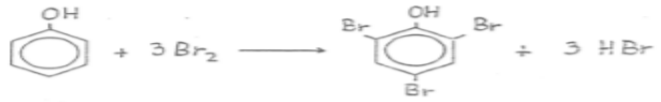
Very small concentration of Iodine can be detected by its own colour or using starch solution as indicator. Starch– Amylose + Amylopectin. Amylose straight chain compound, gives blue colour with Iodine

Disadvantageous- Insoluble in Cold water, instability of suspension in cold water, gives water insoluble complex with Iodine, which means indicator has to be added late, just before the end point

- **Applications:**

1. Determination of Fe(III): $2\ Fe^{3+} + 2I \rightarrow 2Fe^{2+} + I_2$
2. Determination of Cu(II): $2\ Cu^{2+} + 4I^- \rightarrow 2\ CuI + I_2$
3. Determination of H_2O_2 : $H_2O_2 + 2I^- + 2H^+ \rightarrow I_2 + 2H_2O$
4. Determination of phenol:

   Phenol can be brominated using bromine carried out by the reaction of BrO_3^- standard solution and an adequate amount of Br^-. After this, the excess of bromine is then titrated using Iodometry. That is after, the addition of iodide, the resulting iodine is titrated using thiosulphate.



5. Determination of thiocyanate:

   The reaction of thiocyanate with bromine is quantitative and gives BrCN

$$SCN + 4\ Br_2 + 4\ H_2O \rightarrow BrCN + SO_4^{2-} + 7\ Br^- + 8H^+$$

   The needed amount of bromine is added as bromine water and its excess is removed by addition of enough of phenol. The bromine cyanide is measured by Iodometry.

$$BrCN + 2\ I^- \rightarrow I_2 + Br^- + CN^-$$

❖ **Ceriometry Titration:**

Principle: Oxidation-reduction titrations involving cerium sulphate as an oxidizing agent is called as ceriometry titration. Cerium sulphate is powerful oxidant and can be used only in acidic solution. In natural solution ceric hydroxide (hydrous cerci oxide) or basic salts precipitate. Cerium salts have intense yellow color and end point detection can be possible without any indicator in hot solution

Advantageous:

1. Cerium (IV) solutions are stable over prolonged period. They need not be protected from light, and may be even boiled for a short time without appreciable change in concentration.
2. Cerium sulphate can be used to determine the reducing agents in presence of high concentration of HCl. This an advantage over $KMnO_4$
3. Cerium (IV) solutions in 0.1M solutions are not too highly colored to obstruct vision when reading meniscus in burettes.
4. In reaction of Cerium (IV) salts in acid solution with reducing agent, simple change takes place. Permanganate leads to several reduction products

$$Ce^{4+} + e^- \rightarrow Ce^{3+}$$

Detection of end point: Detection of end point can be possible by ceric salts acting as its own indicator. But in addition to this, various internal (redox) indicators are used for detection of end point. N-phenylanthranillic acid, ferroin, 5,6-dimethyl ferroin are used for detection of end point…….

Preparation of 0.1 M cerium sulphate:

Molecular weight of cerium sulphate and cerium ammonium sulphate are 333.25 and 632.57 respectively. Weigh 35 gm of cerium sulphate add 56 mL of sulphuric acid and stir with frequent water addition and gentle warming to dissolve salt completely. Transfer to volumetric flask and cool, dilute to one litre mark with distilled water.

Preparation of 0.1 M cerium ammonium sulphate:

Dissolve 65 gm of cerium ammonium sulphate with the help of gentle heat, in a mixture of 30 mL of H_2SO_4 and 500 mL of water, cool and filter if turbid and dilute it to 1000 mL of water.

Standardization with arsenic trioxide

Weigh accurately about 0.2 gm of arsenic trioxide, previously dried at 105 ^oC for 1 hour and transfer to 500 mL of conical flask. Wash with 25 mL of 8 % w/v solution of sodium hydroxide, swirl to dissolve, add 100 mL of water and mix. Add 30 mL of dilute sulphuric acid, 0.15 mL of osmic acid solution, 0.1 mL of ferroin solution and titrate with cerium ammonium sulphate, slowly the pink color changes to vary pale blue.

❖ **Applications:**

Determination of As(III)

In the presence of 3 drops of OsO_4 in suphuric acid medium direct determination by the following reaction is possible (indicator is ferroin):

$$2\ Ce^{4+} + AsO_3^{3-} + H_2O \rightarrow 2\ Ce^{3+} + AsO_4^{3-} + 2\ H^+$$

Determination of hydrogen peroxide

Hydrogen-peroxide also directly reacts with Ce(IV) ions (indicator is ferroin):

$$2\ Ce^{4+} + H_2O_2 \rightarrow 2\ Ce^{3+} + O_2 + 2\ H^+$$

❖ **Dichrometry Titration**

Principle: Dichromate titrations or titrations with potassium dichromate in acidic solution are based on the conversion of dichromate ion containing hexavalent chromium into tivalent chromium ions.

$$Cr_2O_7^{-2} + 14\ H^+ + 6e \rightarrow 2Cr^{+++} + 7\ H_2O$$

Although potassium dichromate is not powerful oxidizing agent as potassium permanganate, it has several advantages over potassium permanganate…..

1. It is available in pure form
2. Its stable
3. Aq. solutions are sufficiently stable provided that they are store properly.

The equivalent weight is one sixth of the molecular weight, i.e.

Equivalent weight= 294.22/6 = 49.03

End Point Detection:

- The end point in dichromate titration can be possible either by use of external indicator or by internal indicator
- Potassium ferricyanide was widely used as external indicator before use of internal indicator. Oxidation of acidified ferrous solution is titrated with the potassium dichromate solution. Potassium ferricyanide indicator is placed on white tile.
- If the solution of reaction mixture before the end point is placed on indicator solution, deep blue color is produced. Completion of titration is shown when there is no change in color in the mixed drops.
- Redox indicator is used for the detection of end point in dichromate titrations. 1% solution of diphenylamine in concentrated sulphuric acid, 1% solution of diphenyl benzidine in conc. Sulphuric acid and 0.2 % aq. solution of sodium diphenylamine sulphonate are sued.

Preparation and standardization of Potassium dichromate

- Potassium dichromate is an excellent primary standard substance as it is available in a pure grade and stable.

Preparation of 0.0167 M potassium dichromate:

Weigh 4.9 gm of potassium dichromate previously powdered and dried in desiccator for 4, and dissolve in water to produce 1000 mL.

Standardization:

To 20 mL of solution, add 1 gm of potassium iodide and 7 mL of 2M hydrochloric acid. Add 250 mL of water and titrate with 0.1 M sodium thiosulphate using 3 mL of starch solution until the color changes from blue to light green

Factor:

Each mL of 0.1 M sodium thiosulphate is equivalent to 0.0049 gm of $K_2Cr_2O_7$