

UNIT: III PRECIPITATION TITRATION, COMPLEXOMETRIC TITRATION,
GRAVIMETRY AND DIAZOTISATION TITRATION

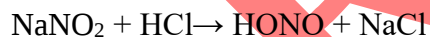
CLASS:30

TOPIC: DIAZOTISATION TITRATION

Diazotization is used in the analysis of aromatic compounds containing an amino group in the molecules. This analysis is based on the reaction between aromatic primary amine ($-\text{NH}_2$), and HONO , in the presence of excess mineral or inorganic acids.

NaNO_2 is generally used in the direct method of diazotization. It gives HNO_2 in an acidic solution. Many aromatic primary amines with free $-\text{NH}_2$ group can be analyzed quantitatively by measuring the volume of NaNO_2 solution required to convert them into diazonium salts.

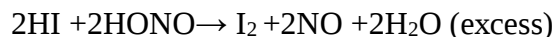
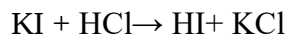
The typical reaction of diazotization reaction in the presence of HCl is given as:



When all the aromatic amines have reacted with NaNO_2 , the next portion (excess) of NaNO_2 is added to the solution under test, and converted to HONO , which remains in the solution and can be detected by the starch paper or paste as an external indicator.

This appearance of free HNO_2 in solution indicates that the diazotization reaction is complete and that the equivalence point has been attained.

Starch iodide paper or paste is the starch solution plus an equal volume of 5% KI solution in H_2O . Starch iodide paste with reaction mixture is as follows



I_2 + Starch blue color (endpoint)

The liberated I_2 reacts with starch to give a blue color. The diazotization proceeds quantitatively only in the presence of inorganic acid. It is important to check the acidity at the end of the titration. If there is no excess of acid present, starch-iodide paper will not detect excess HNO_2 and so will not indicate the endpoint.

There are mainly three types of methods based on the titration procedure. They are as follows:

1. Direct method: The main principle involved in this method is to treat the amino group containing the drug with the acid solution. The resulting solution is immersed in the cold-water bath or ice water bath by maintaining the temperature at 0–5 °C. Then this solution is titrated with the sodium nitrite solution. The endpoint is determined by the above-mentioned methods.
2. Indirect method: The principle involved in this method is that the excess nitrous acid is added to the titration sample solution and it is back titrated with the other appropriate titrant. This method is mainly used for the titration of insoluble diazonium salts.
3. Other method: The main principle involved in this method is the formation of the diazo oxide which is more stable than the diazo compounds. For example, the aminophenol is readily oxidized by the nitrous acid and converted to quinones in the presence of copper sulphate solution and forms the diazo oxide compounds. This readily undergoes the coupling reaction with the nitrous acid.

Preparation and Standardization of 0.1M sodium nitrite solution

Preparation of 0.1M sodium nitrite solution:

- 7.5 g of sodium nitrite is dissolved in sufficient water to produce 1000 ml

Standardization of 0.1M sodium nitrite solution

- About 0.5 g of sulphanilamide (previously dried at 105 °C for three hours) is transferred to a suitable beaker
- 50 ml of water and 20 ml of HCl is added, stirred until it dissolves
- Cooled to 15 °C
- Contents of the beaker are titrated against 0.1M sodium nitrite solution
- Each ml of 0.1M sodium nitrite solution = 0.01722 g of sulphanilamide

Diazotization Titration:

- The specified amount of drug is dissolved in about 50 ml of water and 20 ml of HCl
- Solution is stirred and cooled to about 15 °C
- Mixture is titrated against 0.1M sodium nitrite solution
- Endpoint is determined by
- Using external indicator- starch iodide paper
- Electrometric technique by using platinum electrodes

Applications of diazotization titrations:

1. Direct titration with sodium nitrite solution

- Benzocaine
- Dapsone
- Primaquine phosphate
- Procaine

- All sulpha drugs containing free aromatic amino group like sulfacetamide, sulfadiazine, sulfamethoxazole, etc

2. Conversion of amino group by chemical reactions

A. By reduction

- Metronidazole
- Secnidazole
- Chloramphenicol
- These drugs contain nitro group
- Can be reduced by using any reducing agent to get primary amino group
- Primary aromatic amino group can be diazotized by sodium nitrite

B. Hydrolysis

- Paracetamol (acetyl derivative)
- Phthalyl sulphathiazole (phthalyl derivative)
- Succinyl sulphathiazole (succinyl derivative)
- These drugs are derivatives of amino groups
- Like acetyl or phthalyl or succinyl derivative
- After hydrolysis the free amino group can be titrated with sodium nitrite
- Isocarboxazid- acid solution of the drug liberates benzylhydrazine which can be diazotized to give benzylazide.