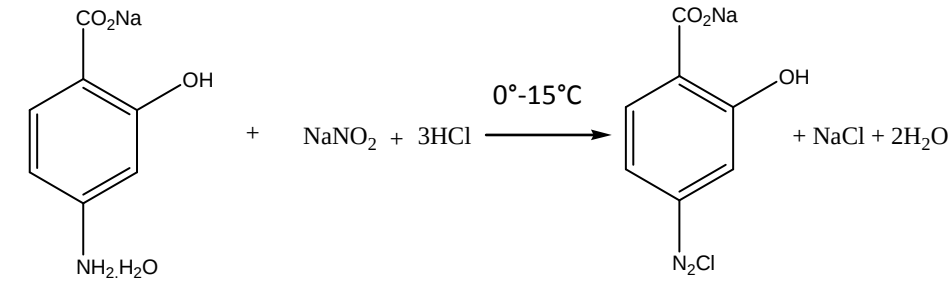
Sodium nitrite titration/ Diazotization Titration

Principle: Aromatic primary amine react with $NaNO_2$ in acidic solution under cold condition (0°-15°C) to form diazonium salt/compound.

$$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{0°\text{-}15°C} C_6H_5N_2Cl + NaCl + 2H_2O$$



Sodium amino salicylate Diazo

It is quantitative reaction under controlled condition & is used to determine most of substances containing a free primary amino group. (as in sulphonamide & other sulpha drugs).

End point is observed by determining small excess of HNO_2 acid which is then present and is seen visibly by starch-Iodide paper or paste as external indicator.

$$KI + HCl \longrightarrow HI + KCl$$

$$2HI + 2HNO_2 \longrightarrow I_2 + 2NO + 2H_2O$$

Liberated I_2 reacts with starch $\longrightarrow$ blue color

Alternative determination is done by amperometric method. It uses pair of platinum electrode, immersed in titration liquid. When small voltage of 30-50mV is applied across the electrodes, polarization of electrodes takes place, and now no current flows through the galvanometer.

At the end point, liberation of HNO_2 depolarizes the electrodes, and current flows in galvanometer with permanent deflection of galvanometer needle. This point is known as dead stop end point.

Examples of drugs analysed by Diazotization titration: Benzocaine, Dapsone, Sulphacetamide sodium, Primaquine phosphate, procaine HCl, Sulphadimidine etc.

PREPARATION OF 0.1 M SODIUM NITRITE SOLUTION

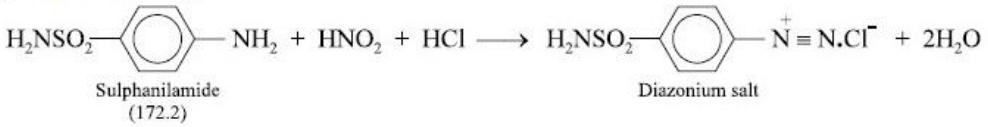
Weigh accurately 7.5 g of sodium nitrite and add sufficient DW to produce 1 litre in a 1000 ml volumetric flask.

STANDARDIZATION OF 0.1 M SODIUM NITRITE SOLUTIOlN WITH SULPHANILAMIDE

Materials Required : Sulphanilamide (previously dried at 105°C for 3 hours) : 0.5 g ; hydrochloric acid (~ 11.5 N) : 20 ml ; 0.1 M sodium nitrite.

Theory : The nitrous acid, generated on the introduction of sodium nitrite solution into the acidic reaction mixture, reacts with the primary amino group of sulphanilamide quantitatively, resulting into the formation of an unstable nitrite that decomposes ultimately with the formation of a diazonium salt. The diazonium salt thus produced is also unstable, and if the reaction mixture is not maintained between 5-10°C, it shall undergo decomposition thereby forming phenol products which may react further with nitrous acid. The reactions involving the formation of the diazonium salt may be expressed in the following manner :

$$NaNO_2 + HCl \rightarrow HNO_2 + NaCl$$



Sulphanilamide (172.2) — Diazonium salt

$$C_6H_8N_2O_2S \equiv NaNO_2$$

or $172.2\ g\ C_6H_8N_2O_2S \equiv 1000\ ml\ M$

or $17.22\ g\ C_6H_8N_2O_2S \equiv 1000\ ml\ 0.1\ M$

or $0.01722\ g\ C_6H_8N_2O_2S \equiv 1\ ml\ of\ 0.1\ M\ NaNO_2$

Procedure : Weigh accurately 0.5 g of suphanilamide and transfer to a beaker. Add to it 20 ml of hydrochloric acid and 50 ml of DW, stir until dissolved and cool to 15°C in an ice-bath. Add to it 25 g of crushed ice, and titrate slowly with sodium nitrite solution, stirring vigorously, until the tip of the glass rod dipped into the titrated solution immediately produces a distinct blue ring on being touched to starch-iodide paper. The titration is supposed to be complete when the end-point is seen after the resulting mixture has been allowed to stand for 1 minute. Each 0.01722 g of sulphanilamide is equivalent to 1 ml of 0.1 N sodium nitrite.