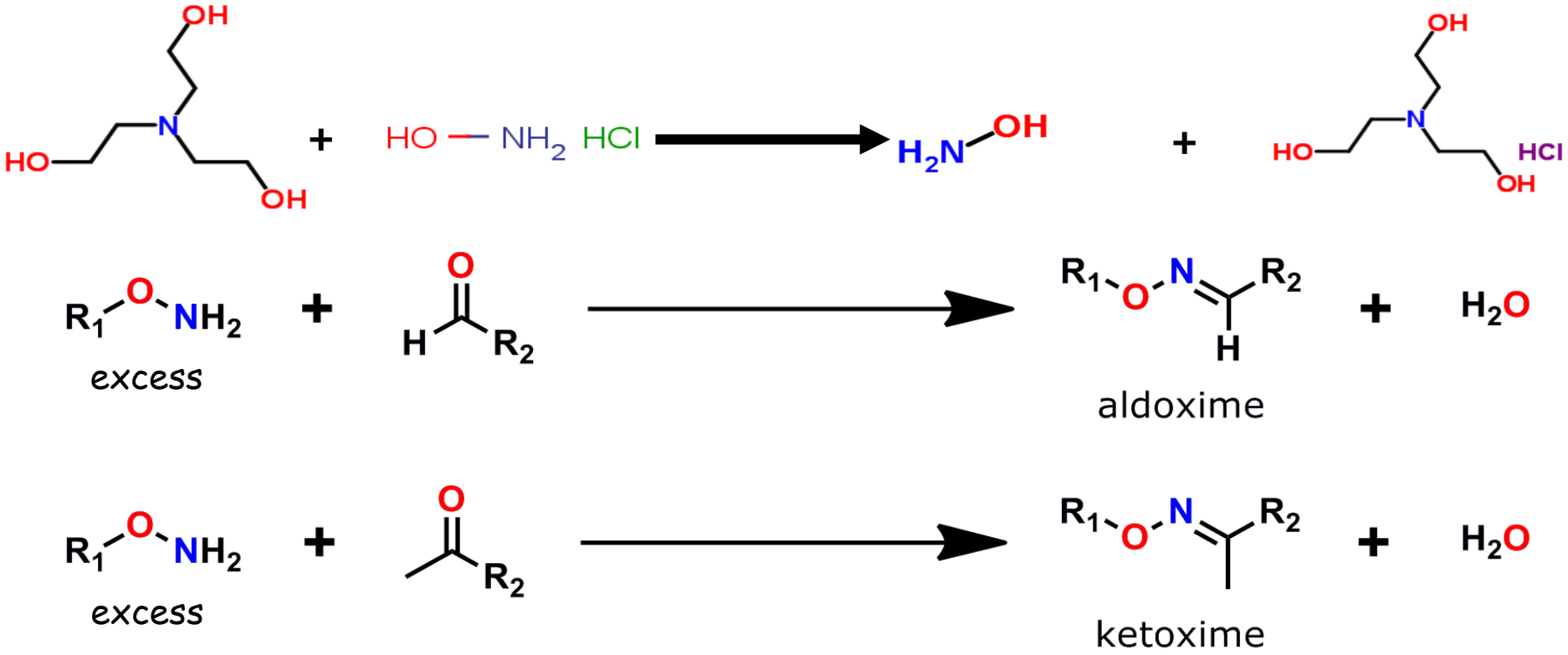
ORGANIC MICROANALYSIS

- **Microanalysis** is the chemical identification and quantitative analysis of very small amounts of chemical substances (generally less than 10 mg or 1 ml) or very small surfaces of material (generally less than 1 cm^2). It consists of:

  - Carbonyl compounds
  - Hydroxyl compounds
  - Carboxyl compounds
  - Amino compounds
  - Alkoxy and Oxyalklene compounds
  - Epoxide compounds
  - Anhydrides compounds
  - Unsaturated compounds
  - Diazonium salts
  - Hydrazides
  - Mercaptans
  - Dialkyl disulfides
  - Dialkyl sulfides
  - Sulfoxides
  - Sulfonates

Carbonyl compounds

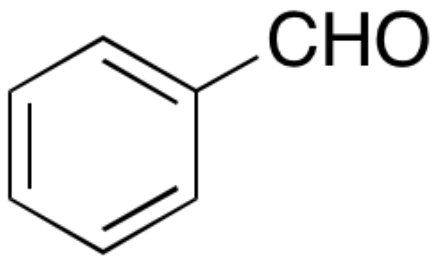
Oxime formation: Hydroxylamine hydrochloride

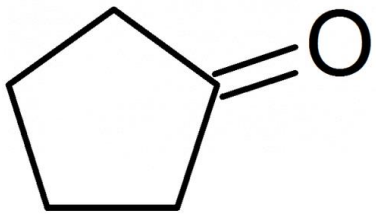


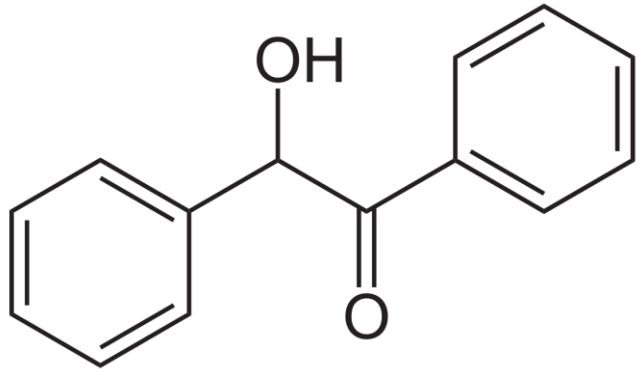
- In this method, unreacted quantity of NH_2OH is determined by titration with HCl using bromophenol blue as an indicator in a medium consists of (50% water:50% 2-propanol)

Oxime formation: Hydroxylamine formate

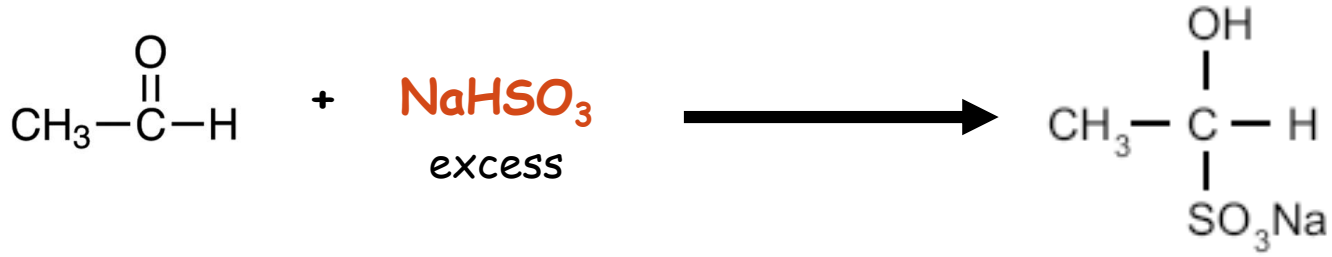
- In this method, unreacted quantity of $H_2N\text{-}OH.HCOOH$ is determined by titration with HNO_3 using thymol blue as an indicator.







Addition of sodium bisulphite



- In this method, unreacted quantity of $NaHSO_3$ is determined by the following ways:

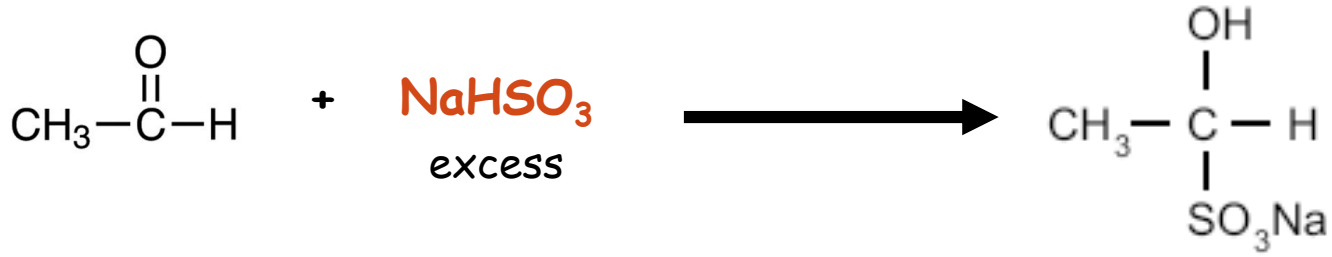
A. Titration against NaOH using phenolphthalein as an indicator.

$$NaHSO_3 + NaOH \xrightarrow{ph.ph} \text{(more than 1 mg).}$$

B. Direct titration against iodine (I_2) using starch as an indicator (iodimetric titration).

$$NaHSO_3 + I_2 \xrightarrow{Starch} \text{(E.P is blue colour).}$$

Addition of sodium bisulphite



- In this method, unreacted quantity of $NaHSO_3$ is determined by the following ways:

C. Indirect titration against ($Na_2S_2O_3$) using starch as an indicator.

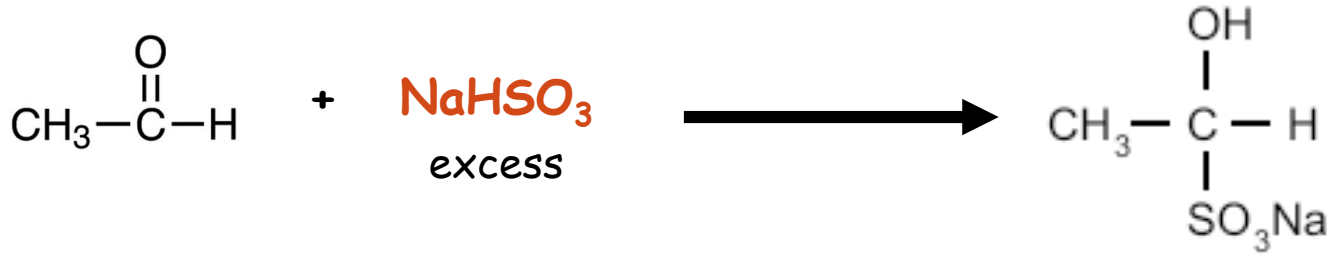
$$NaHSO_3 + I_2 \longrightarrow 2I^-$$

$$I_{2\ (unreacted)} + 2Na_2S_2O_3 \xrightarrow{Starch} Na_2S_4O_6 + 2NaI$$

D. Or spectrophotometric determination of unreacted iodine at selected wavelength.

$$I_{2\ (unreacted)} \xrightarrow{Starch} \text{Blue complex} \quad (\lambda_{max} = 600\ nm)$$

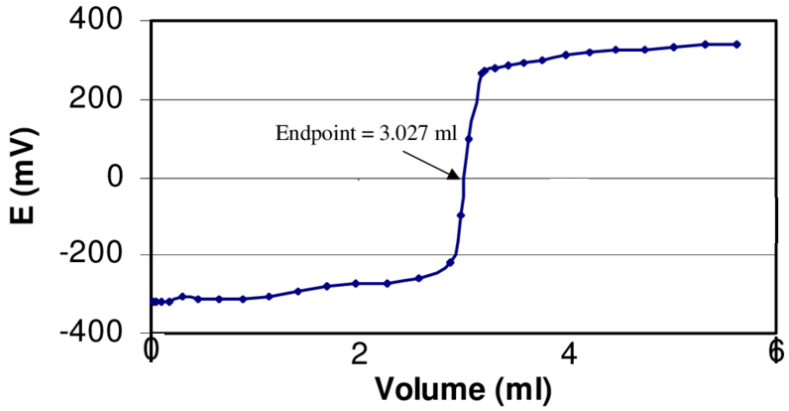
Addition of sodium bisulphite



- In this method, unreacted quantity of $NaHSO_3$ is determined by the following ways:

E. Potentiometric titration against NaOH

This method is used to determine aldehydes more than ketones



Examples: Acetaldehyde, benzaldehyde, and butanal

Addition of hydrazine

Hydrazine excess

Hydrazone

- Hydrazone is extracted by petroleum ether.
- Unreacted quantity of hydrazine is determined iodometrically:

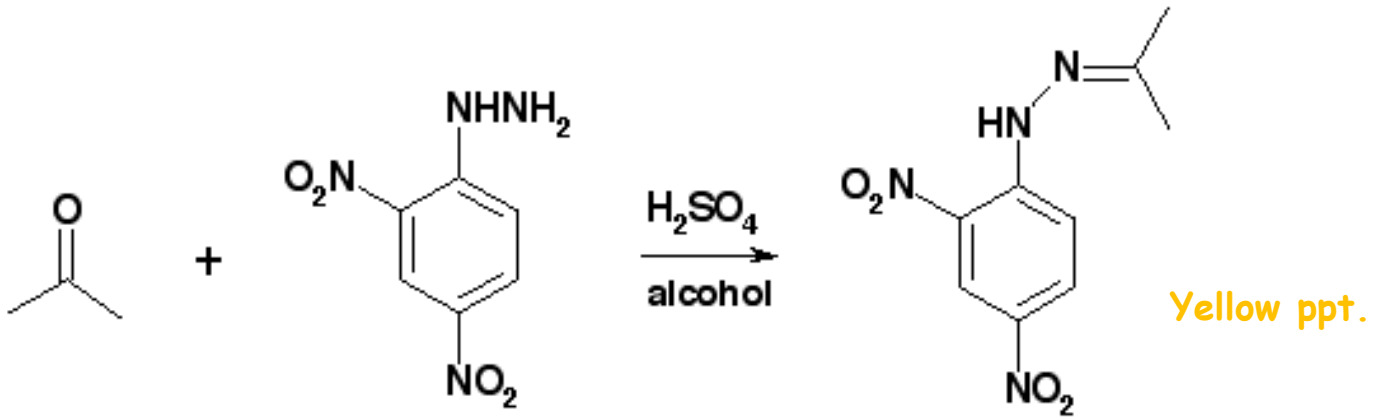
$$H_2NNH_2\ (\text{unreacted}) + I_2 \xrightarrow{\text{Starch}} 2I^-$$

$$H_2NNH_2\ (\text{unreacted}) + I_{2\ \text{excess}} \longrightarrow 2I^-$$

$$I_{2\ (\text{unreacted})} + 2Na_2S_2O_3 \xrightarrow{\text{Starch}} Na_2S_4O_6 + 2NaI$$

$$I_{2\ (\text{unreacted})} \xrightarrow{\text{Starch}} \text{Blue complex}\ (\lambda_{max} = 600\ \text{nm})$$

Addition of 2,4-dinitrophenyl hydrazine



2,4-dinitrophenyl hydrazine

2,4-dinitrophenyl hydrazone

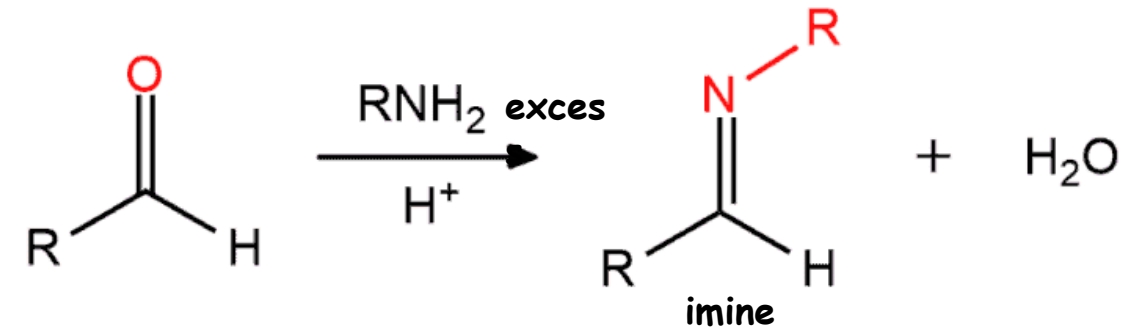
2,4-dinitrophenyl hydrazone can be determined by the following methods:

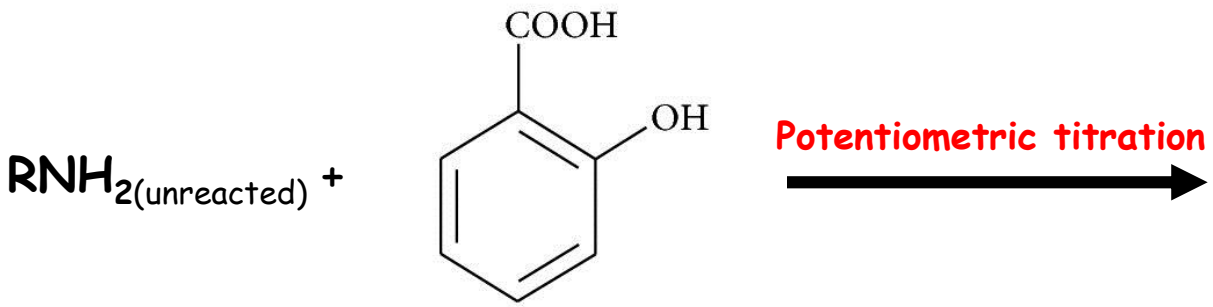
a. Gravimetrically: the dry yellow ppt is weighed.

b. Spectrophotometrically: by adding NaOH to the reaction mixture to form (crimson-red) which determines at λ_{max} =480 nm.

- The produced complex can be extracted by hexane to enhance the sensitivity of the method to be able to detect trace amounts (ppm) of carbonyl compounds.

Schiff base formation

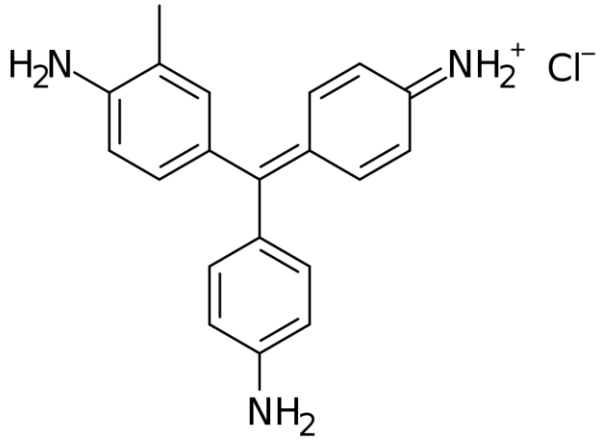


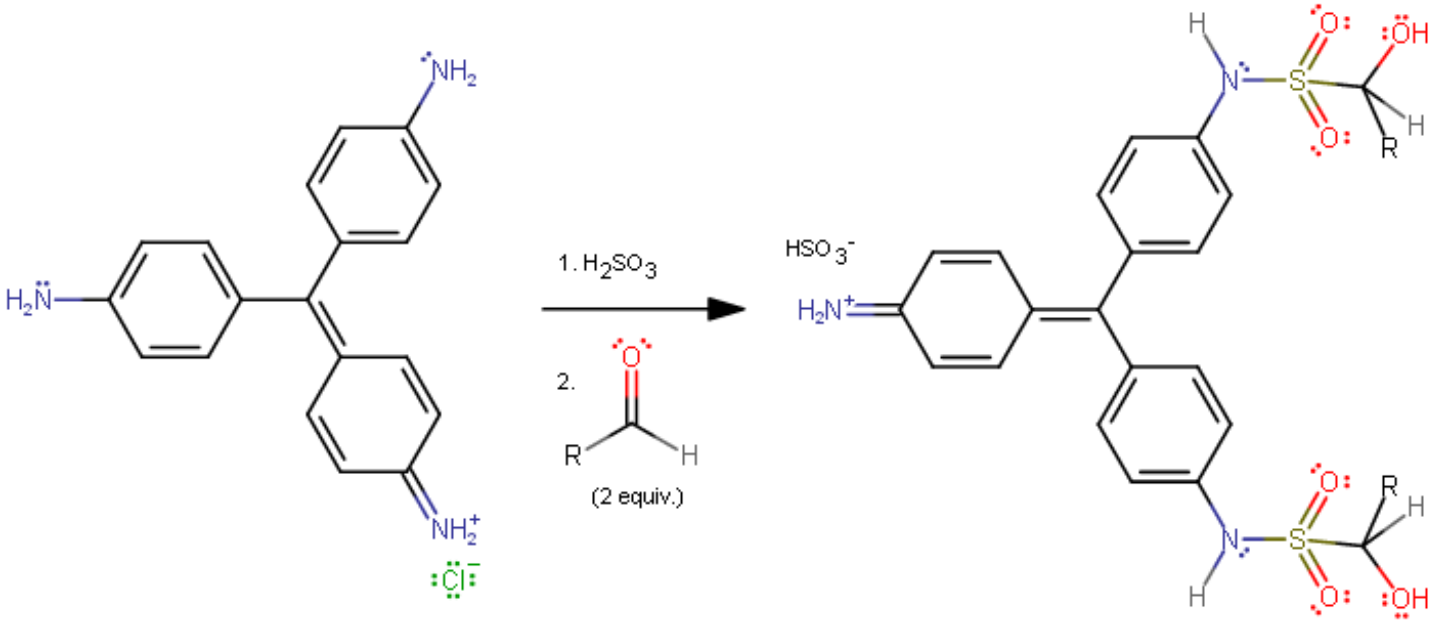


- This method is used to determine aldehydes (aliphatic and aromatic) like formaldehyde, furfural, benzaldehyde

Reaction with Rosaniline.HCl

- This method is used to determine the trace amounts of aldehydes (aliphatic and aromatic) ONLY . So it will be a very good method to recognise between aldehydes and ketones. Aldehydes will form a violet complex when reacting with Rosaniline.HCl, which can be spectrophotometrically measured at λ_{max}= 560 nm





Reaction with Potassium mercuric iodide (K_2HgI_4)

- This method is used to determine the aldehydes (aliphatic and aromatic) in the presence of ketones . Aldehydes react with **mercurial reagent** in alkaline medium.

$$RCHO + K_2HgI_4 + 3KOH \longrightarrow RCOOK + Hg + 4KI + 2H_2O$$

$$RCHO + Hg^{2+} + 2OH \longrightarrow RCOOH + Hg + H_2O$$

- The liberated mercury, which is equivalent to the aldehyde, can be determined by acidify the solution followed by addition of an excess of Iodine. The unreacted amount of iodine can be back titrated later against sodium thiosulfate using starch as an indicator OR direct addition of starch to the excess of iodine will form a blue coloured solution which can be determined spectrophotometrically at λmax= 600 nm

$$Hg + I_{2\ (excess)} \longrightarrow HgI_2$$

$$I_{2\ (unreacted)} + 2Na_2S_2O_3 \xrightarrow{Starch} Na_2S_4O_6 + 2NaI$$

$$I_{2(unreacted)} \xrightarrow{Starch} \text{Blue coloured solution } (\lambda_{max} = 600 \text{ nm})$$

Reaction with Silver nitrate ($AgNO_3$)

- Tollens' test, also known as silver-mirror test, is used to determine the aldehydes (aliphatic and aromatic) in the presence or absence of ketones . Aldehydes react with **known excess of $AgNO_3$** in alkaline medium.

$$2AgNO_3 \xrightarrow{NaOH} Ag_2O$$

$$RCHO + Ag_2O \longrightarrow RCOOH + 2Ag \text{ (silver-mirror)}$$

- The unreacted silver nitrate can be determined by titration with ammonium thiocyanate with Fe(III) as indicator in acidic medium (Volhard method).

$$2AgNO_3 + NH_4SCN \longrightarrow AgSCN + NH_4NO_3$$

$$NH_4SCN_{(unreacted)} + Fe^{3+} \longrightarrow [Fe(SCN)]^{2+}$$

Red solution

- OR by using Atomic absorption spectroscopy (AAS)

Polarographic determination of carbonyl compounds

- An electrochemical technique used in analytical chemistry, polarography is electrolysis using a dropping mercury electrode (DME). The technique enables the obtaining of current-voltage curves from which the concentration of many species can be determined with high reproducibility at very low concentrations.

- It is required to have a reducible functional group in the organic compounds in order to give a polarographic wave when that group is reduced at DME.

- Carbonyl groups in aldehyde and ketones can be determined by polarography as it considered a reducible group.

Using hypoiodite (OI^-)

- It has limited applications because of the interferences that take place by most of organic compounds which have the ability to be oxidised by a powerful oxidising agent (hypoiodite).

$$RCHO + \underset{\text{excess}}{I_2} + NaOH \longrightarrow RCHO + \underset{\text{excess}}{OI^-} \longrightarrow COOH$$

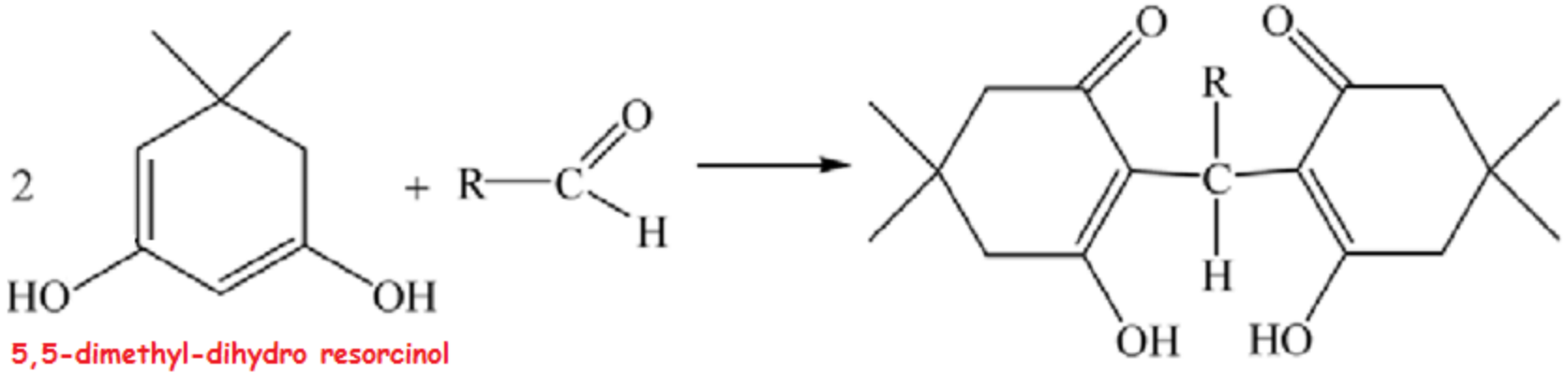
$$\underset{\text{unreacted}}{OI^-} \xrightarrow{H^+} I_2$$

$$I_{2\ (\text{unreacted})} + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI$$

$$I_{2(\text{unreacted})} \longrightarrow \text{Blue coloured solution } (\lambda_{max} = 600\ nm)$$

Using Methone method

- This method is used to determine the aldehydes (aliphatic and aromatic) in the presence of ketones. Aldehydes react with **methon (also known Dimedon method)**.



5,5-dimethyl-dihydro resorcinol

- The resulted compound is a dibasic acid which can be titrated with a suitable base.

Hydrolysis of Acetal, ketal, imine