Assay of Magnesium Sulfate

$MgSO_4 . 7H_2O$

Mwt.=246.5gm/mole

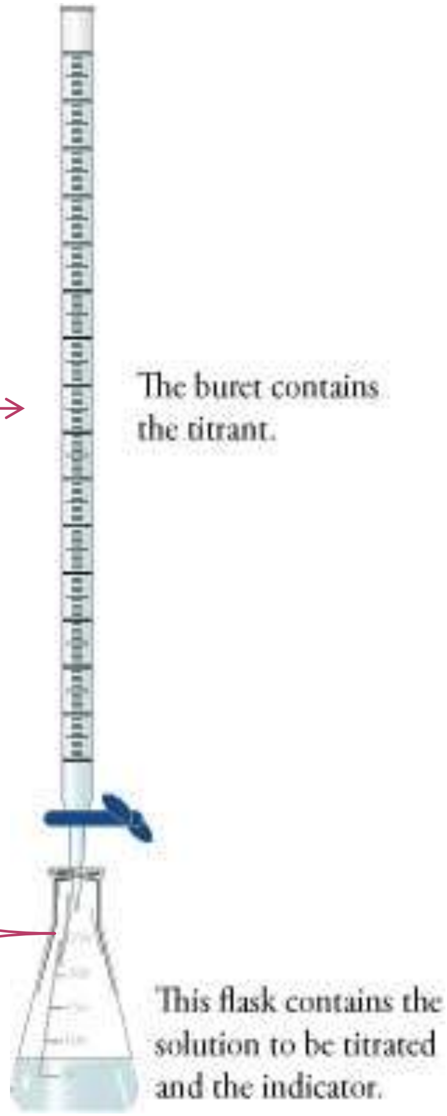
- Contain not less than 99.5% $MgSO_4$ calculated with reference of dried substance.
- Description: colorless crystal, or white crystal powder.
- Solubility: soluble at 20˚C in 1.5 parts of water, sparingly soluble in alcohol 96% i.e. practically insoluble in 96% ethanol.
- Uses: laxative agent.

- **Assay:**

Each 1ml of M/20 EDTA≡0.012325gm $MgSO_4.7H_2O$

***Note*:**

End point from pink to blue or bluish violet



The buret contains the titrant.

This flask contains the solution to be titrated and the indicator.

M/20 EDTA →

10ml unknown
10ml buffer
0.1gm mordant black indicator

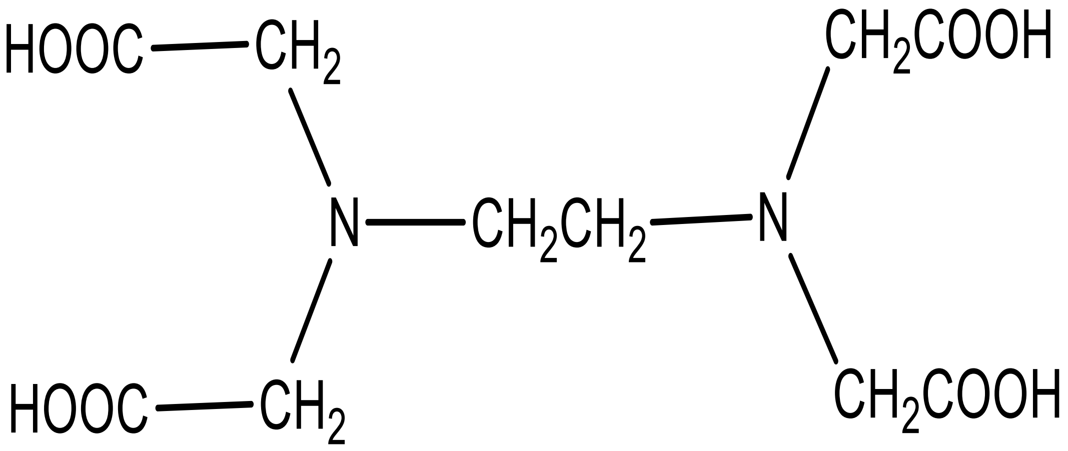
- The technique involves titrating *metal ions* with a *complexing agent* or *chelating agent (Ligand)* and is commonly referred to as ***complexometric titration***. This method represents the analytical application of a complexation reaction.
- In this type of titration we use ***metal ion indicator***.
- **Chemical principle**:

- It is type of complexometric titration.

$$MgSO_4 + Na_2H_2EDTA \rightleftharpoons (MgEDTA)^{=} + 2H^{+} + Na_2SO_4$$

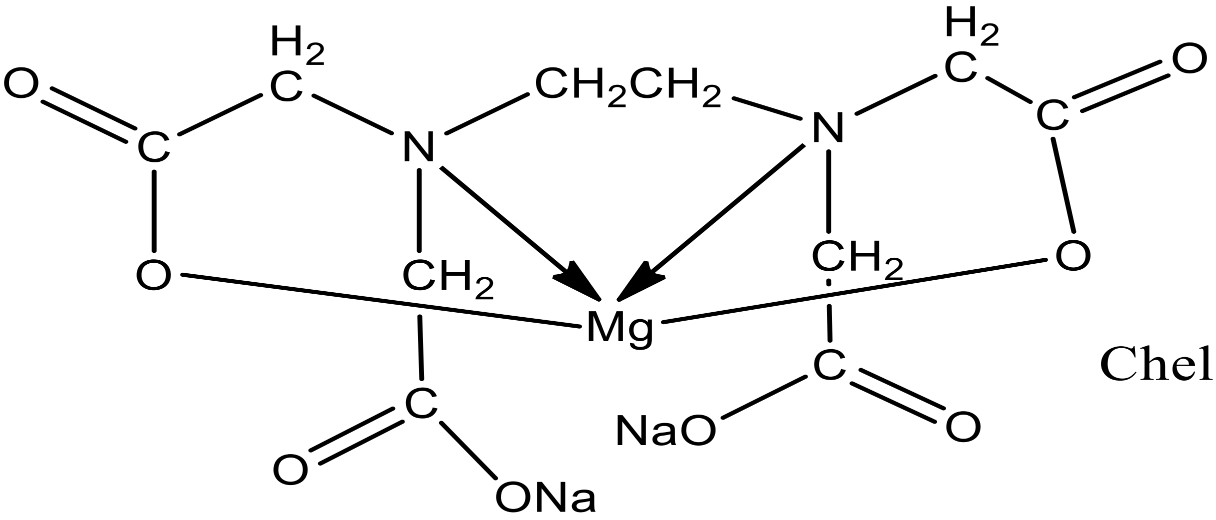
- Magnesium ions form relatively weak complex with (EDTA ;Ethylenediaminetetra-acetic acid).
- The stability of metal complex is pH dependent. Lower the pH of the solution, lesser would be the stability of complex (because more H^+ ions are available to compete with the metal ions for ligand)
- But at pH 10 the reaction is rapid and quantitative .

- NH_3- NH_4Cl buffer is used to maintain this pH.
- EDTA which is polyamine carboxylic acid is one of the most frequently used chelating agent:



EDTA

- EDTA form soluble, stable 1:1 chelates with metal ion.



Chelate

- Because of the low water solubility of the free acid form of EDTA, the disodium salt (Disodium EDTA) is used in preparation of std. sol.
- **Indicator: Metal Indicator**
- Metal indicators are used to detect the end point in complexometric titration.
- They are dyes which produce one color in the presence of metal ions and a different color when they are absent.
- The color changes are the result of displacement of the H^+ ions by the metal.
- The metal indicator form 1:1 complex (MI) which must be weaker than the Metal-EDTA complex.

$$M + I \rightleftharpoons MI$$

$$M + EDTA \rightleftharpoons M\text{-}EDTA$$

$$\underset{\text{pink}}{MI} + EDTA \rightleftharpoons M\text{-}EDTA + \underset{\text{blue}}{I}$$

- **Chemical factor:** it forms 1:1 chelate so;

  1Mwt. $MgSO_4.7H_2O \equiv$ 1Mwt. EDTA

0.012325gm $MgSO_4.7H_2O \equiv$ 1ml of M/20 EDTA

- **Chemical principle:**

- At the onset of titration, the buffered reaction media contains the MI complex and free M:

$$M + I \rightleftharpoons MI$$

- When the titrant (EDTA) is added to the system, it will progressively chelate the free metal ions in the solution, and then a competitive reaction will take place, 1:1metal ions and EDTA, since the MI complex is weaker than M_EDTA.

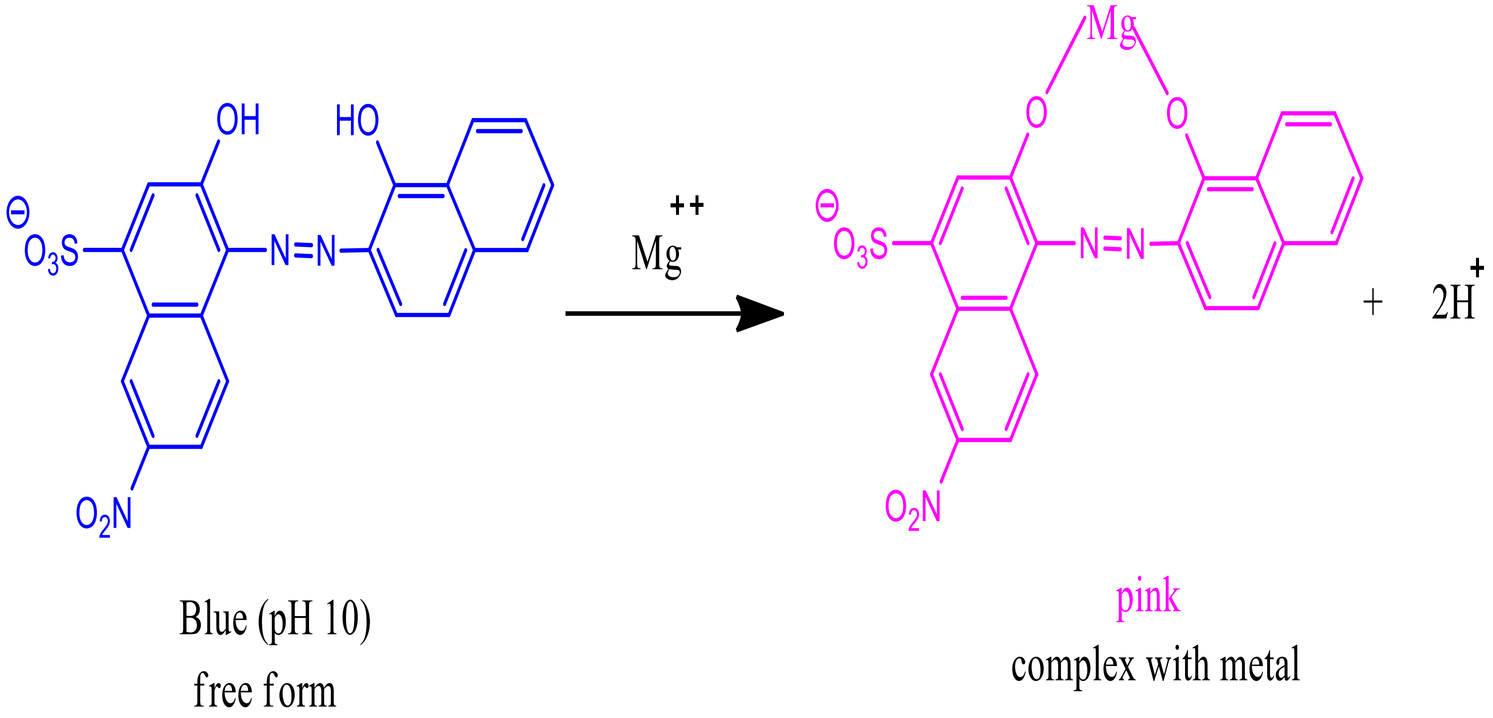
- Finally, at the equivalent point, EDTA removes the last traces of metal ions from its colored complex with ind.(MI) to free metal ind.(I) of another color.

$$\mathrm{M} + \mathrm{EDTA} \rightleftharpoons \mathrm{M\text{-}EDTA}$$

$$\underset{\text{pink}}{\mathrm{MI}} + \mathrm{EDTA} \rightleftharpoons \mathrm{M\text{-}EDTA} + \underset{\text{blue}}{\mathrm{I}}$$

- **Mordant black indicator:** it has blue color at pH10 and most of its complexes are reddish.

Note: In pH less than *6.3* and more than *11.5*, the indicator and its complexes are reddish, so it is necessary to carry out the titration in the presence of ***buffer at pH 10***.



- **Calculation:**

  V × ch. factor= gm wt. of $MgSO_4.7H_2O$

  wt × 100/10= %w/v of unknown.

ASSAY OF BORAX

Borax or Sod. borate or

Sod. Tetraborate

Chemical formula $Na_2B_4O_7.10H_2O$

Mwt.= 381.4 gm

- **Physical properties**: Borax is sod.tetraborate decahydrated, should be kept in well closed container, soluble in 20 parts of water.
- **Uses**; antiseptic and astringent in mouth paints.
- **Procedure**: 10mL of unknown

  10mL of distilled water

  2drops of methyl red indicator

Titrate with *N*/2 HCl solution, the color of sol. changes from yellow → pink–orange(**1st end point**).

❋Record the volume of *N*/2 HCl consumed.

Boil and cool the solution,

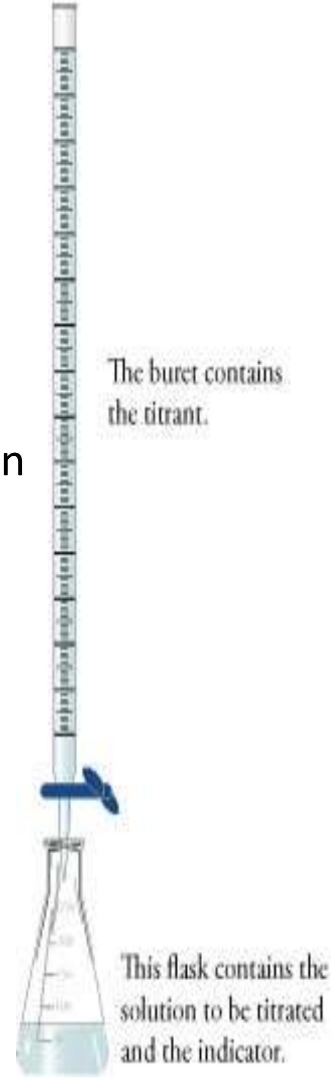
Add 4gm mannitol and 2drops of phenolphthalein ind. The color of sol. is pink

Now titrate with *N*/1 NaOH until the color of sol. changes from pink → yellow → pink(**2nd end point**).

- Record the volume of *N*/1 NaOH consumed.

1st titration

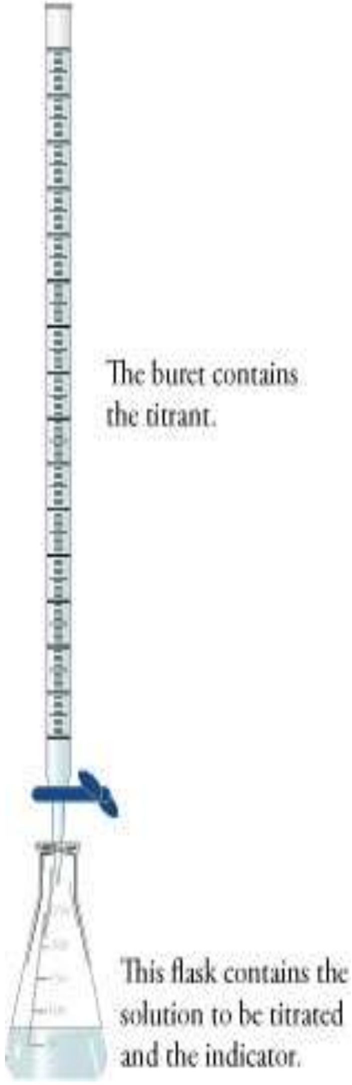
N/2 HCl solution



10mL of unknown
10mL of D.W
2drops of methyl red indicator

2nd titration

N/1 NaOH solution



Boil , cool and add
4gm mannitol and
2drops of ph.ph ind.

- **Chemical principle:**

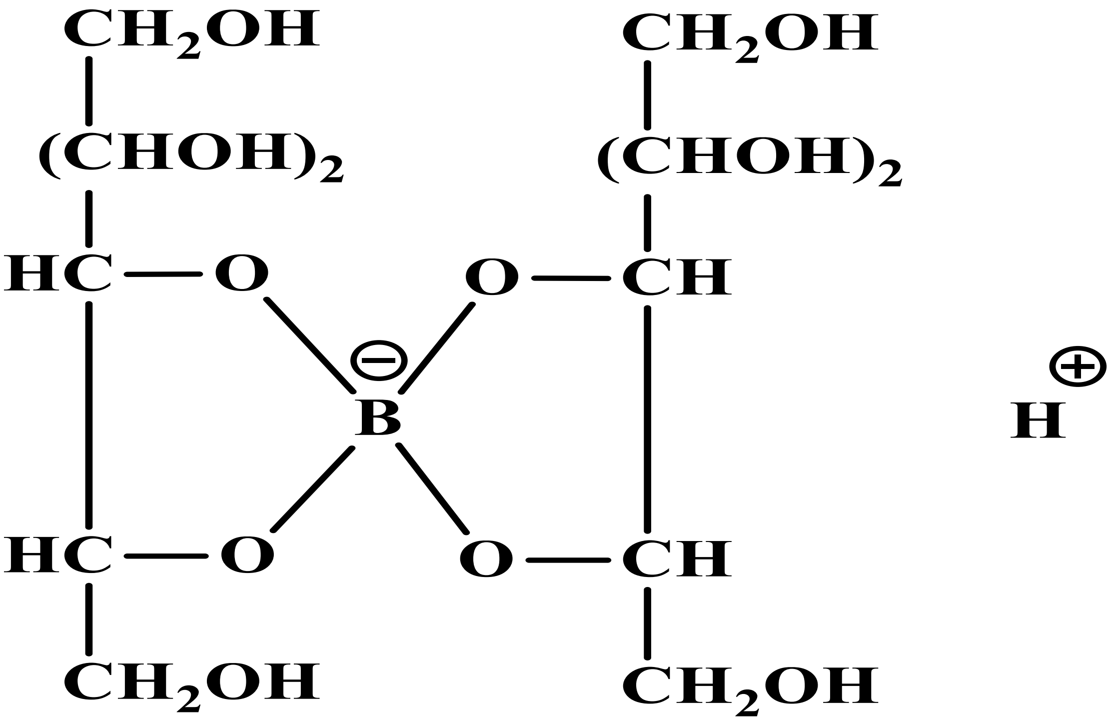
- Borax is a salt of weak acid with strong base.

  $Na_2B_4O_7.10H_2O + 2HCl \longrightarrow 2NaCl + 4H_3BO_3 + 5H_2O$

- Boric acid(H_3BO_3) will be liberated, it is very weak acid.
- Boil the solution to remove CO_2 .
- Add mannitol because boric acid is weak acid to convert it into strong complex acid which is strong enough to be titrated directly with NaOH.
- Mannitol should be used in high conc. to prevent the hydrolysis of the complex.

$$4H_3BO_3 + 4NaOH \xrightarrow{\text{Mannitol}} \underset{\text{sod. metaborate}}{4NaBO_2} + 8H_2O$$

- Mannitol should be used in high conc. to prevent the hydrolysis of this complex.



mannityl boric acid

- **Chemical factor:** ***home work***

- For borax with 0.5*N* HCl (0.09535 gm)
- For borax with 1*N* NaOH (0.09535 gm)
- For sod. carbonate with 0.5*N* HCl (0.0265gm)
- For boric acid with 1*N* NaOH (0.06184gm)

Mwt. Boric acid=61.84 gm/mol

Mwt. Na_2CO_3= 106gm/mol

- **Calculations:**

we must first correct the volume of HCl & NaOH

1. If we have **pure borax**, the vol. of *N*/2 HCl must be equal to the vol. of 1*N* NaOH.

   $V'_{\text{of } N/2 \text{ HCl}} = V'_{\text{of } 1N \text{ NaOH}}$ (the differences up to 0.3 mL)

   take the average of the two volumes & calculate the % w/v of Borax.

2. **Impure borax** may contain Na_2CO_3 or boric acid as impurities.

a) Mixture of **Borax & Na_2CO_3**

   Na_2CO_3 is basic; it can react with HCl, so both borax and carbonate will react with HCl

   $Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$

While NaOH react only with boric acid liberated from borax. Then after vol. correction;

V_1 of *N*/2 HCl > V_2 of 1*N* NaOH

V_1- V_2= vol. of *N*/2 HCl react with Na_2CO_3

Calculate the % w/v for Borax and Na_2CO_3.

b) Mixture of **Borax & boric acid**

$$Na_2B_4O_7.10H_2O + 2HCl \longrightarrow 2NaCl + \underbrace{4H_3BO_3}_{\text{liberated boric acid}} + 5H_2O$$

$$\underbrace{H_3BO_3}_{\text{Liberated \& free boric acid}} + NaOH \xrightarrow[\text{Mannitol}]{} NaBO_2 + 2H_2O$$

So both the liberated and free boric acid react with NaOH,then

Correct the volumes and compare:

V_2 of 1*N* NaOH $>$ V_1 of *N*/2 HCl

$V_2 - V_1$ = vol. of 1*N* NaOH react with free boric acid

Calculate the % w/v for Borax and free boric acid.

Assay of Chlorinated lime

Or bleaching powder

Or Ca. Chlorohypochlorite [Ca(OCl)Cl]

Assay of Chlorinated lime

[Ca(OCl)Cl]

- Contain not less than 30%w/w available chlorine.
- It is dull-white powder with characteristic odor, partially soluble in water and in 96% ethanol.
- Used as disinfectant.

Procedure:

The flask used in the titration is ***iodine flask***

≈0.1N $Na_2S_2O_3$

10ml of unknown
1.5gm KI
5ml of 33%v/v HAC

note: starch is added near the end point when the color of the solution changed from brown to yellow.

* **End point is colorless**

- Chemical principle:

$$Ca(OCl)\,Cl + 2CH_3COOH \longrightarrow (CH_3COO)_2Ca + HOCl + HCl$$

hypoclorous acid

$$HOCl + HCl \longrightarrow Cl_2 + H_2O$$

available chlorine

The *available chlorine* is the Cl_2 which is liberated from the substance by the action of acid.

This liberated chlorine will displace an equivalent amount of I_2 from KI.

$$Cl_2 + 2KI \longrightarrow 2KCl + I_2$$

The liberated I_2 is titrated against sod. thiosulfate using starch mucilage as indicator.

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

Chemical factor:

1ml of 0.1N $Na_2S_2O_3 \equiv$ 0.003545gm *available chlorine.*

Calculation:

Correct the sod. thiosulfate volume=V’

V’ X ch. factor= gm of *available chlorine* in 10ml.

(Gm/10)X100= %w/v of *available chlorine.*

Assay of copper sulfate

Cupric sulfate $CuSO_4.5H_2O$

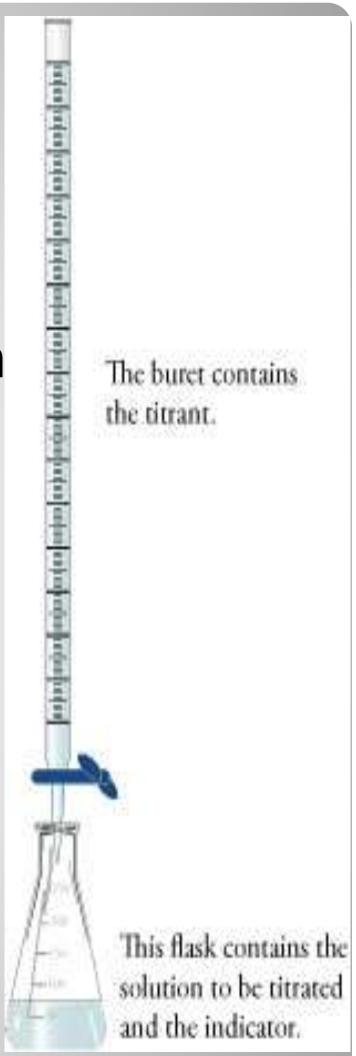
Mwt.=249.68 gm

- **Properties**: blue, fine prism or blue crystalline powder.
- **Solubility**: soluble at 20°c in 3parts of water and 3parts of glycerol, almost insoluble in 95% alcohol.

  It contains not less than 98.5% and not more than 101%w/w $CuSO_4.5H_2O$.
- **Uses**: as fungicide.

- **Procedure:** the titration should be carried in stoppered flask.

During titration the color of the solution changed from ***brown*** to ***faint yellow*** then add1ml starch and 1gm KSCN and complete titration.



≈0.1N **$Na_2S_2O_3$**

10ml unknown
30ml D.w.
1.5 gm KI
5ml acetic acid

- **Chemical principle:**

- $CuSO_4$ is treated with excess KI in acidic media.

oxidizing agent acidic media

$$2CuSO_4 + 4KI \longrightarrow 2CuI_2 + 2K_2SO_4$$

- The formed Cupric iodide(CuI_2) is unstable.
- CuI_2 will break into cuprous iodide(CuI or Cu_2I_2) and I_2.

$$2CuI_2 \longrightarrow 2CuI(Cu_2I_2)\downarrow + I_2$$

unstable yellow ppt.

- The liberated I_2 is titrated with std. $Na_2S_2O_3$ sol.

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

- **Notes:**

1. KI is added to liberate I_2.
2. Excess KI is added to dissolve I_2.
3. HAC is added to make the medium slightly acidic.
4. In acidic media the liberated I_2 is adsorbed by the ppted CuI.
5. KSCN(pot. thiocyanate) is added near the end point.

$$KSCN + CuI \longrightarrow CuSCN + KI$$

this KI will return to react with $CuSO_4 \rightarrow \rightarrow I_2$

- **Chemical factor:**

1ml of 0.1N $Na_2S_2O_3 \equiv$ 0.02497gm $CuSO_4.5H_2O$

- **Calculation:**

- ☐ correct the volume of $Na_2S_2O_3$=V’
- ☐ V’ X Ch. Factor= gm wt. of $CuSO_4.5H_2O$ in 10ml
- ☐ (Gm/10) X 100= %w/v of $CuSO_4.5H_2O$ in the unknown

Assay of Ferrous Sulfate

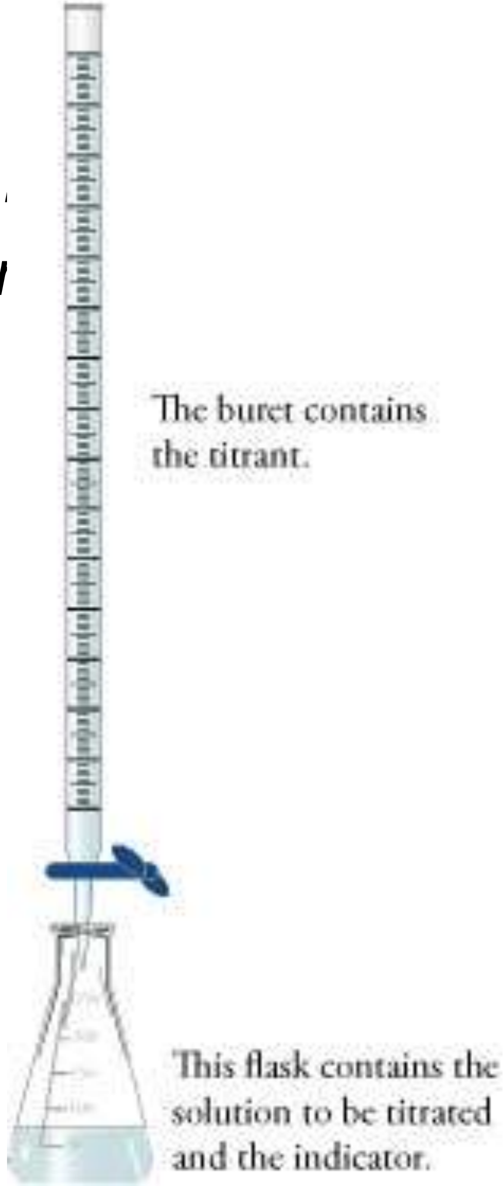
$FeSO_4.7H_2O$

Mwt.=278gm/mole

- **Appearance**: The blue-green heptahydrate is the most common form of ferrous sulfate ,it is bluish green crystals, freely soluble in water.
- **Content**: Ferrous Sulfate (crystal) contains 98.0－104.0% of ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$)
- **Used** in the prevention and treatment of iron deficiency.

- **Procedure:**

H_2SO_4 should be added to maintain a
constant H ions concentration as explai



$\approx 0.1\text{N } KMnO_4$

Unknown powder
20ml of diluted H2SO4

End point: colorless → ***pink***

- **Chemical principle:**

$10FeSO_4+2KMnO_4+8H_2SO_4 \rightarrow 2MnSO_4+5Fe_2(SO_4)_3+K_2SO_4+$
$8H_2O$

Or $MnO_4^{-} +8\,H^{+}+5Fe^{+2} \rightarrow Mn^{+2} +4H_2O+5\,Fe^{+3}$

- Ferrous sulfate is a ***reducing agent***.
- It will be titrated against standard solution of potassium permanganate(***oxidizing agent***) in acidic media.
- ***Note***: you must write the oxidation and reduction equations by each.
- **Chemical factor:**

Derive the ch. Factor from the previous chemical equation.

$1ml.\ of\ 0.1N\ KMnO_4 \equiv 0.0278gm\ of\ FeSO_4$

- **Calculation**:

Correct the volume of $KMnO_4$ consumed=V'

Then multiply the corrected volume (V') by the Ch. Factor.

to get the weight;

V' x ch. Factor =gm of $FeSO_4$ in the unknown.

Assay of Hydrogen Peroxide

H_2O_2

H_2O_2: Mwt.=34.02 gm/mole Different H_2O_2 solution: 30%,27%w/w and 6%, 3%w/v

- H_2O_2 is slightly more viscous than water.
- Aqueous solution of H_2O_2 colorless and odorless. Rapidly decomposes when contact with organic matter and certain metals; Cu, Fe, Mn and if allowed to stay in alkaline solution. $2H_2O_2 \rightarrow O_2 + H_2O$

- In acidic solution Fe^{2+} is oxidized to Fe^{3+} (H_2O_2 acting as an oxidizing agent):

  $2\,Fe^{2+} + H_2O_2 + 2H^+ \rightarrow 2\,Fe^{3+} + 2H_2O$

- hydrogen peroxide acts as a reducing agent in its reaction with $KMnO_4$ *in our experiment*.

  $2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 2Mn^{2+} + 5O_2 + 8H_2O$

- **Uses:**

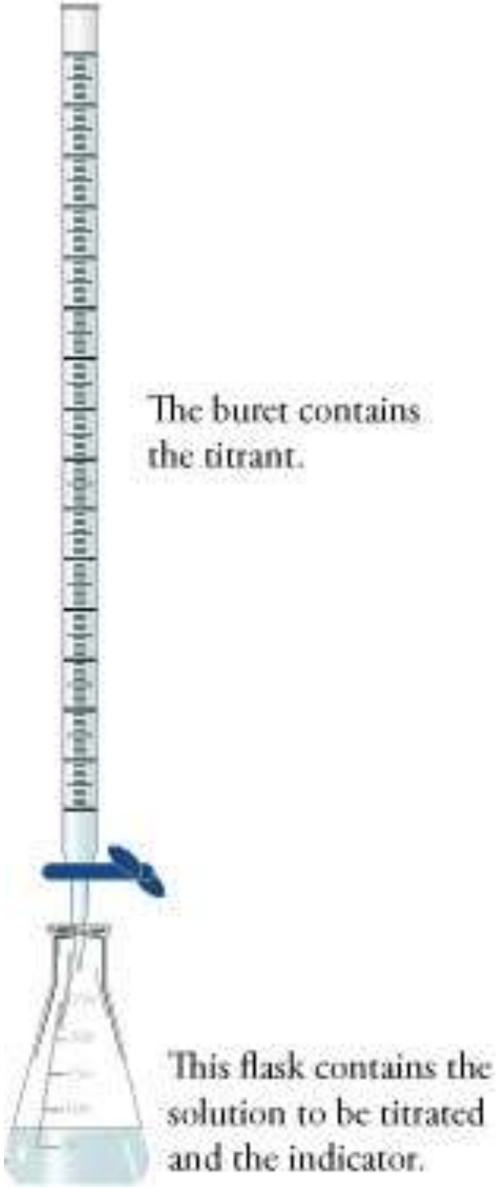
  It is a ***disinfectant*** or ***antiseptic*** for treating wounds for its antimicrobial activity.

  it is an effective ***cleaning agent*** prevents infection transmission in the hospital environment.

Procedure:

≈ 0.1N $KMnO_4$ →

10ml of unknown
25ml of D.W.
5ml of 50%v/v H_2SO_4



End point: *colorless → pink*

- **Notes:**

1. We make the media acidic **to;**
   - Prevent decomposition of H_2O_2
   - Prevent reaction of $KMnO_4 \rightarrow MnO_2$
   - Increase oxidizing power of $KMnO_4$
2. Titration should be done slowly

- **Chemical principle:**

$2KMnO_4+5H_2O_2+3H_2SO_4 \longrightarrow K_2SO_4+2MnSO_4+5O_2+8H_2O$

You must write the oxidation and reduction equations to calculate the eqwt. for both $KMnO_4$ & H_2O_2 .

- **Chemical factor:**

According to the chemical equation;

2Mwt of $KMnO_4 \equiv$ 5Mwt of H_2O_2

then complete the derivation of the Ch. Factor.

The Chemical factor is equal to:

1ml of 0.1N $KMnO_4 \equiv$ 0.001701gm of H_2O_2

- **Calculation:**
- Correct the **volume** of $KMnO_4$

  NxV = *N'xV'* (corrected)
- Multiply the corrected volume by the Ch. Factor.

  to get the **weight (wt.)** of H_2O_2
- the **%w/v** of H_2O_2 = **wt**. /10 x 100

- There is 2 methods to calculate the concentration of hydrogen peroxide in commercial products:

1. %W/V:

10ml of concentrated sol. was diluted to 200ml with D.W. → Then 20ml is taken from the dil. one and titrated with approximately 0.1N $KMnO_4$

conc.	diluted
10	200
x	20

x= 20X10/200=1ml of conc. sol. (original sol.)

Correct the volume of $KMnO_4$= ***Vol.***

Vol. x ch. Factor =wt. of H_2O_2 in 1ml.

Then calculate %w/v

2. **Volume strength of the solution:**

Decomposition occurs according to this equation:

$$2\,H_2O_2 \longrightarrow 2\,H_2O + O_2$$

Example: if the %w/v of H_2O_2 is 8.5%w/v ***i.e.*** It contains 8.5 gm of H_2O_2 in 100ml solution.

wt.	Vol.
8.5	100ml
X	1ml (from the definition)

X= 0.085 gm of H_2O_2 in 1ml

$$\underline{2\,H_2O_2} \longrightarrow 2\,H_2O + \underline{O_2}$$

2 × 34gm mwt.	22400ml
0.085gm	y

y = 28ml of O_2

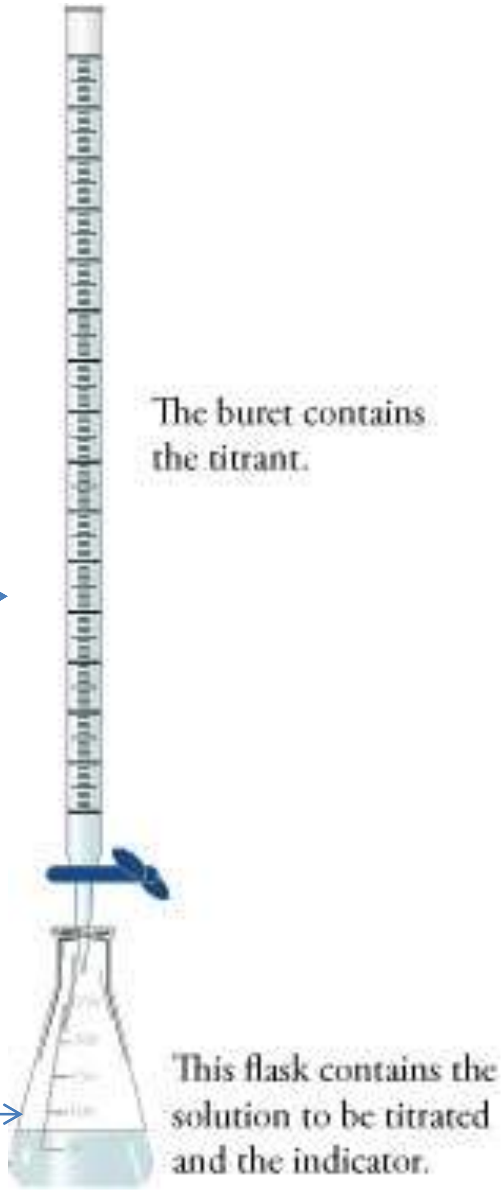
So the *volume strength* of the sample is 28.

Assay of sodium hydroxide solution

NaOH solution

- From B.p, NaOH solution contains not less than 97.5% w/w of total alkali (as NaOH) and not more than 2.5 % w/w Na_2CO_3.
- **Assay:**

- 10 ml of unknown(bulb pipette).
- 25 ml of distilled water.
- Add 2.5 ml of barium chloride solution.
- Titrate with 1N HCl solution using 1-2 drops of phenolphthalein ind..
- The first end point from pink → colorless(turbid)
- To the turbid sol. add 5 drops of Bromophenol Blue ind. and complete titration with 1N HCl .
- The second end point bluish violet → yellowish green



The buret contains the titrant.

This flask contains the solution to be titrated and the indicator.

1N HCl solution

10 ml of unknown
25ml of D.W
2.5 ml of $BaCl_2$ solution
1-2 drops of ph.ph. ind. (1st titration)
5-6 drops of B.p.B ind. (2nd titration)

Chemical principle:

- NaOH is strong base, absorbs CO_2

$$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$$

- both NaOH and Na_2CO_3 react with HCl

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$$

When we assay a sample, we do the assay for total alkalinity contributed to NaOH and Na_2CO_3.

- Barium chloride ($BaCl_2$) is added to precipitate all carbonate

$$\underset{\text{soluble in alkaline}}{BaCl_2 + Na_2CO_3} \longrightarrow \underset{\text{insoluble in alkaline}}{BaCO_3\downarrow} + 2NaCl$$

- ***1st titration***:

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

Why HCl do not react with $BaCO_3$?

Why the end point is turbid?

- ***2nd titration***:

$$2HCl + BaCO_3 \longrightarrow BaCl_2 + H_2O + CO_2$$

definition of <u>chemical factor</u>: the weight of substance that is chemically equivalent to 1ml of std. solution.

- **Calculation of the *chemical factor*:**

a) From reaction of HCl with NaOH:

1Mwt of NaOH $\equiv$ 1 Mwt HCl

1 Mwt of NaOH $\equiv$ 1 eqwt HCL

1 × 40 gm of NaOH $\equiv$ 1 liter of 1N HCl

40/1000 gm NaOH $\equiv$ 1ml of 1N HCl

0.04 gm of NaOH $\equiv$ 1ml of 1N HCl of total alkalinity calculated as NaOH(chemical factor)

b) From reaction of 2HCl with Na_2CO_3

2Mwt of HCl $\equiv$1Mwt of $BaCO_3$ $\equiv$1Mwt Na_2CO_3

1Mwt Na_2CO_3 $\equiv$ 2Mwt of HCl

1Mwt Na_2CO_3 $\equiv$ 2 eqwt of HCl

½ Mwt Na_2CO_3 $\equiv$ 1 eqwt of HCl

106/2 gm Na_2CO_3 $\equiv$ 1liter of 1*N* HCL

53 gm Na_2CO_3 $\equiv$ 1liter of 1*N* HCL

53/1000 gm Na_2CO_3 $\equiv$ 1ml of 1*N* HCL

0.053 gm Na_2CO_3 $\equiv$ 1ml of 1*N* HCL (chemical factor)

- **Calculations** :

V_1 is the of HCl consumed in the 1st titration

V_2 is the of HCl consumed in the 2nd titration

$V_1+V_2= V_3$ total HCl consumed.

correct the V_3 according to this equation:

$V \times N= V' \times N'$

Corrected $V_3 \times 0.04=$ gm wt. of total alkali

Then the % w/v of total alkali

Corrected $V_2 \times 0.053=$ gm wt. of Na_2CO_3

Then the % w/v of Na_2CO_3 in the unknown

Preparation & Standardization of ≈ 0.1 N Potassium Permanganate ($KMnO_4$) solution

Redox Reaction

- ***Preparation of ≈ 0.1N $KMnO_4$ solution:***

- Dissolve 3.3 gm of solid $KMnO_4$ in 1000ml. distilled water, in a flask.
- Heat the solution on a hotplate for 15min. at 70-80 °c.
- Cool the solution to room temp. and allow stand for 2 days in a dark place.
- Filter the solution through the glass wool or asbestos before use.

Standardization of $KMnO_4$ solution:

- *Filter the prepared soln. through glass wool as said before.*
- *Rinse and Fill the burette with filtered $KMnO_4$ soln.*
- *Weigh accurately about 200mg sod. oxalate ($Na_2C_2O_4$), previously dried at 110 °c to constant weight.*
- *Dissolve it with 100ml of D.W. in a conical flask. Add 7ml. of conc. H_2SO_4.*
- *Heat the soln. to about 70°c.*
- *Titrate against $KMnO_4$ soln. until a permanent pale pink color appear (persist for 15 sec.).*
- *Record the volume of $KMnO_4$ consumed.*

- ## OXIDATION- REDUCTION REACTIONS:

❖ Methods of analysis involve a change in valence of the reacting substances, thus there is always a transfer of electrons.

❖ Electrons lost by reducing agent are gained by oxidizing agent. The oxidizing agent will be reduced; gain of electrons and then decreasing in oxidation number, but the reducing agent will be oxidized; losing of electrons and then increasing in oxidation number.

- We can calculate the eqwt. of the reactants:

$$\text{Eq. wt} = \frac{\text{Mwt.}}{\text{no. of e- gained or lost by each molecule}}$$

- ***Permanganate* ion** (MnO_4^-) acts as an oxidizing agent in acidic media, being reduced to Mn^{++}:

$$\overset{+7}{Mn}O_4^- + 8H^+ + 5e^- \longrightarrow Mn^{+2} + 4H_2O$$

- Oxalate ion ($C_2O_4^=$)acts as reducing agent:

$$C_2O_4^= \longrightarrow 2CO_2 + 2e^-$$

- $KMnO_4$ is widely used in volumetric analysis as a standard and oxidizing agent because:

1. It is strong oxidizing agent.
2. The intense color of $KMnO_4$ solution is sufficient to signal the end point in most titrations thus it is used as self indicator.

- On the other hand,

1) $KMnO_4$ is a strong oxidizing agent, then it will oxidize any organic matter present in D.W., so heating for 15min. is to accelerate the oxidation of these organic matter.

2) $KMnO_4$ soln. is allowed to stand for 2days to ensure the completion of the decomposition reaction.

3) It is filtered through asbestos to remove all traces of manganese dioxide (MnO_2) .

4) $KMnO_4$ is unstable in the presence of direct sunlight, organic matter ex. Filter paper.

5) H_2SO_4 is added since $KMnO_4$ is better oxidizing agent in acidic media, H_2SO_4 is added to keep $[H^+]$ion conc. constant through out the titration.

6) Heat to about 70 ◦c because the oxidation of sod. oxalate is rapid enough if the temp. above 60 ◦c .

- Sod. oxalate, not oxalic acid, is used because:

1. The salt can be obtained in very pure condition.
2. Free from water of crystallization.
3. It can be dried to 130 ◦c without decomposition.
4. Stable to air.

The chemical equation for the std. of pot. Permanganate:

$$5Na_2C_2O_4 + 2KMnO_4 + 8H_2SO_4 \longrightarrow 2MnSO_4 + 5Na_2SO_4 + K_2SO_4 + 8H_2O + 10CO_2$$

Calculations

$KMnO_4$ $Na_2C_2O_4$

$$N \times V = \frac{WT}{eqwt} \times 1000$$

67gm/mole

The preparation and standardization of 0.1N sodium thiosulfate

$Na_2S_2O_3.5H_2O$

Preparation:

Dissolve about 26gm sod. thiosulfate and 200mg sod. carbonate in 1000ml of recently boiled and cooled D.W.

Standardization:

Put into the stoppered flask the followings;

0.1-0.2 gm of potassium dichromate ($K_2Cr_2O_7$)

100ml of D.W.

3gm potassium iodide (KI)

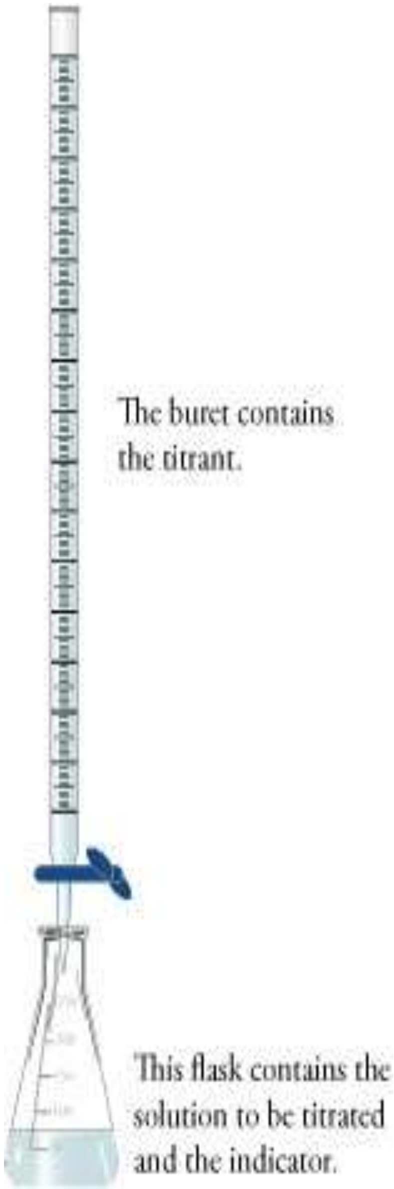
2gm sod. Bicarbonate($NaHCO_3$)

5ml conc. HCl

- Close the flask with the stopper and swirl to mix.
- Then keep the flask in dark place for 10min.

- Rinse the stopper and inner walls of the flask with D.W.
- Titrate the liberated I_2 with sod. thiosulfate the color change from brown to faint yellow.
- Add 1ml of starch indicator the color of the solution change to dark blue.
- Complete titration until the color change to green-blue.

≈ 0.1N $Na_2S_2O_3$



End point: **dark blue** → green-blue

Notes for preparation:

- *Why do we use recently boiled and cooled water?*

  a. to destroy sulfur bacteria

  b. to expel CO_2

$$Na_2S_2O_3 + 2H_2CO_3 \longrightarrow 2NaHCO_3 + H_2S_2O_3$$

$$\begin{tikzcd} H_2S_2O_3 \arrow[r] & H_2SO_3 \arrow[d] & + S\Downarrow \\ & SO_2 + H_2O & \end{tikzcd}$$

thiosulfuric acid

sulfar

- *Na_2CO_3 is added to the solution as preservative*

Chemical principle of standardization:

- Pot. Dichromate is an oxidizing agent

$K_2Cr_2O_7 + 6KI + 14HCl \longrightarrow 3I_2 + 2CrCl_3 + 8KCl + 7H_2O$

- The liberated I_2 is titrated against $Na_2S_2O_3$

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

sod. tetrathionate

- This indirect procedure is known as *iodometry*.

Notes for standardization:

1. We use stoppered flask to prevent the loss of I_2 .
2. KI is added to liberate I_2.
3. Excess KI is added, Why?

$I^- + I_2 \longrightarrow I_3^-$ tri-iodide ion *(soluble form of iodine)*

4. The standardization should be carried in acidic media and not in alkaline media:

because alkaline media I_2 will react with OH^- to give:

$I_2 + OH^- \longrightarrow HI + IO^-$ Hypoiodite ion

$3\,IO^- \longrightarrow IO_3^- + 2I^-$

These ions will oxidize the thiosulfate to:

$$IO^{-} + IO_3^{-} + \underset{\text{thiosulfate}}{S_2O_3^{=}} \longrightarrow \underset{\text{sulfate}}{SO_4^{=}}$$

5. On the other hand in higher acidic media the excess KI will react with HCl to give HI, HI will be oxidized by atmospheric O_2 to I_2:

$$\underset{\text{excess}}{KI} + HCl \longrightarrow HI + KCl$$

$$HI \xrightarrow{\text{atmospheric } O_2} I_2$$

Sod. bicarbonate is added to react with formed HI:

$$NaHCO_3 + HI \longrightarrow NaI + H_2O + CO_2 \nearrow$$

6. We put the flask in dark place for 10min.?
7. Starch ind. is added at the end (when the color of the solution change to yellowish green) or we can said the ind. is added when the iodine concentration is low because β-amylase which the soluble form of starch react :

   $\beta\text{-amylase} + I_2 + I^- \longrightarrow$ blue colour complex

   the color change is reversible, the color being discharged (change to colorless) when iodine is reduced by $Na_2S_2O_3$.

   This reversibility is reduced when the iodine conc. is high for this reason starch ind. should be added until most of I_2 has been reduced by $Na_2S_2O_3$.

8. The end point is a pale green and not colorless why?

Calculation:

$Na_2S_2O_3$ $K_2Cr_2O_7$

$$N \times V = (Wt/eqwt) \times 1000$$

eqwt= 49

The preparation and assay of Aqueous Iodine Solution (Lugol's Solution)

- It contains 5% w/v *Iodine* (limits 4.75- 5.25% w/v) and 10% w/v *Pot. Iodide* (limits 9.5-10.5% w/v).
- Used in pre-operative treatment of thyrotoxicosis.
- **Preparation**:

I_2	50gm
KI	100gm

purified water sufficient to 1000ml

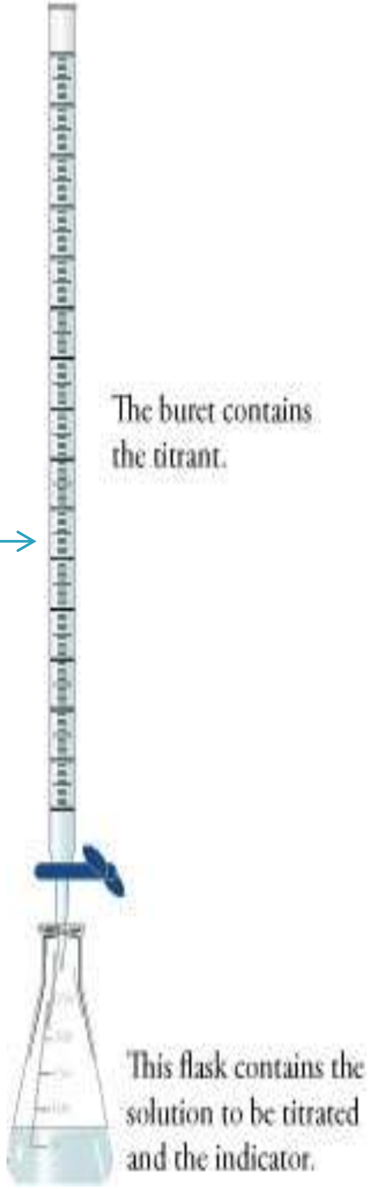
*Dissolve KI in a little amount of water then add the I_2 and shake well until the I_2 is completely dissolved, then add sufficient water to 1000ml using volumetric flask.

- **Assay:** Dilute 25ml of the original sol. to 100ml with distilled water, then:`

a) **Assay of I_2,**

note: *we must use stoppered flask*

Each1ml of N/10 $Na_2S_2O_3 \equiv 0.01269$ gm I_2



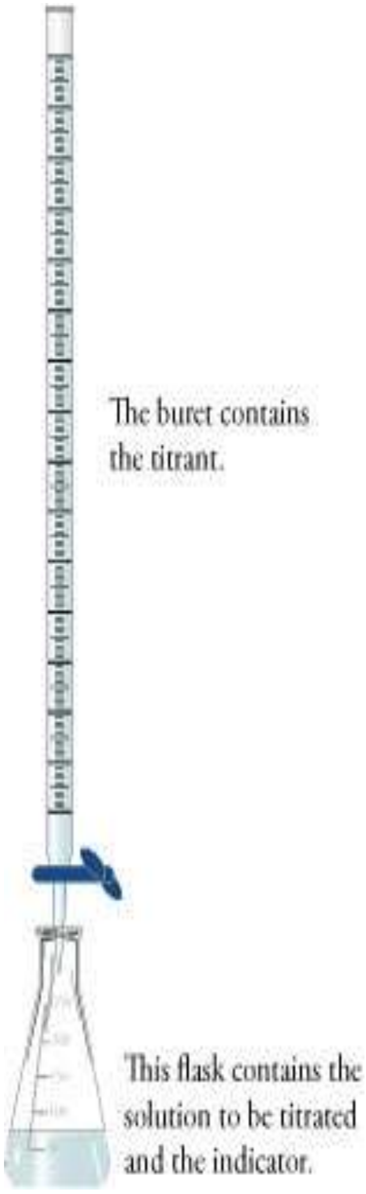
≈ N/10 $Na_2S_2O_3$ →

dark brown, titrate → yellow then add 1ml starch the color change to dark blue complete tit. until the end point colorless

10ml of unknown
10ml D.W

b) Assay of KI,

**titrate with M/20 KIO_3 (Pot. Iodate) until dark brown sol. change to pale brown, add 1ml of <u>amaranth</u> sol.; the color of sol. Change to red and then continue tit. Until the color of sol. change to yellow -orange*



M/20 KIO_3 →

5ml of unknown
10ml D.W
20ml conc. HCl

- From the no. of ml. of M/20 KIO_3 required subtract ¼ no. of ml of N/10 $Na_2S_2O_3$ required in the assay of I_2

  each 1ml of the remainder is≡ 0.0166gm of KI

- Chemical principle for I_2 assay:

  I_2 will oxidize chemically equivalent amount of sod. thiosulfate.

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

- Chemical principle for KI assay:

  KIO_3 (pot. Iodate)is fairly strong oxidizing agent, it can quantitatively react with both iodide I^- and iodine I_2 .

*If the conc. of HCl not exceed 1N the reaction:

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

*In the presence of conc. HCl exceeding 4N, I2 produced by the previous reaction is further oxidized to iodine monochloride (ICl):

$KIO_3 + 2I_2 + 6HCl \longrightarrow KCl + 5ICl + 3H_2O$

* **so** the overall reaction between KIO_3 & KI in the presence of high conc. HCL >4N can be expressed by:

$KIO_3 + 2KI + 6HCl \longrightarrow 3KCl + 3ICl + 3H_2O$

The presence of high conc. HCl is required to decrease :

$HCl + ICl \longrightarrow ICl_2^- + H^+$

stable cpd

- In this experiment we use amaranth indicator, it is a dye, dyes which are destroyed or changed in the presence of oxidizing titrant can be use as indicator.
- We can not use starch as indicator because starch_ iodide complex can not be formed in high acid conc. used in the iodate titration.

- *Chemical factor*: **Homework**

Each1ml of 0.1N $Na_2S_2O_3 \equiv 0.01269$gm of Iodine

Each1ml of M/20 $KIO_3 \equiv 0.0166$gm of KI

Each1ml of M/20 $KIO_3 \equiv 0.02538$gm of iodine

- **Calculation:**
- ***For I2:***

original sol.	Vol.
25	*100*
X	*10*

X= 2.5ml of original sol.

V' x ch.fact. 0.01269x 100/2.5 = %w/v of iodine in orig. sol.

V' the corrected volume of sod. thiosulfate.

- ***For KI:***

original sol.	Vol.
25	*100*
X	*5*

X= 1.25ml of original sol.

$$V_{KIO_3\ M/20} = V_{KIO_3\ M/20\ (used} - \underline{1/4}\ V'_{Na_2S_2O_3}$$

(req. for KI) in the total assay) 0.1N

Vol. of KIO3 (req. for KI)x 0.0166 x 100/1.25= %w/v of KI

- It is preferred to use iodate (KIO_3) of known M rather than of known N, it depends on the nature of reaction.
- KIO_3 sol. used in the titration of sol. containing both iodide and iodine.
- The equivalent of KIO_3 in its reaction with KI differs from its equivalent when react with iodine.