Unit: IV
REDOX TITRATION

By

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Introduction:

- Redox Titration is a laboratory method of determining the concentration of a given analyte by causing a redox reaction between the titrant and the analyte. These types of titrations sometimes require the use of a potentiometer or a redox indicator.
- Redox titration is based on an oxidation-reduction reaction between the titrant and the analyte.
- In order to evaluate redox titrations, the shape of the corresponding titration curve must be obtained. In these types of titration, it proves convenient to monitor the reaction potential instead of monitoring the concentration of a reacting species.

Oxidation & Reduction

Oxidation: A substance can undergo oxidation can occur via:

- The addition of oxygen.
- Removal of hydrogen which was attached to the species.
- The donation/loss of electrons.
- An increase in the oxidation state exhibited by the substance.

$$C + O_2 \rightarrow CO_2$$

(Here carbon has gained oxygen and it has been oxidized to carbon dioxide)

$$Fe^{+2} - e^{-} \rightarrow Fe^{+3}$$

$$Sn^{+2} - 2e^{-} \rightarrow Sn^{+4}$$

- In above reactions, there is loss of electrons, hence the concerned ions are said to be oxidized.

Reduction: A substance can undergo reduction can occur via:

- The addition of hydrogen.
- The removal of oxygen.
- The acceptance of electrons.
- A reduction in the overall oxidation state.

$$CUO + H_2 \rightarrow CU + H_2O$$

- In above reaction, copper oxide has been reduced to copper by loss of oxygen.

$$CU^{+3} + e^{-} \rightarrow CU^{+2}$$

(Here gaining of 1 electron, cupric ion is said to be reduced to cuprous ion.)

What are oxidation-reduction reactions?

- Oxidation-reduction reactions are chemical reactions that involve the transfer of electrons between the reacting species. These electron transfers are accompanied by a change in the oxidation state of the reactants.
- In a chemical reaction, oxidation and reduction occur simultaneously. If one atom is oxidized, other is reduced.

$$\mathbf{Fe^{+2} + Cl_2 \rightarrow 2Fe^{+2} + 2Cl^{-}\ [2(FeCl)]}$$

- In the above reaction, Ferrous ion is oxidized to Ferric ion by loss of 1 electron and Chlorine has been reduced to chloride ion by gain of 1 electron. Therefore, these reactions are called as **redox reactions**.

Oxidizing & Reducing Agents

What are oxidizing agents?

- These are the agents which themselves get reduced i.e. they accept electrons and oxidize other elements. They are also called oxidizer or oxidants.
- Examples: potassium dichromate, potassium permanganate, ceric sulphate, iodine, nitric acid (HNO3) and hydrogen peroxide (H2O2) etc.

What are reducing agents?

- These are the agents which themselves get oxidized i.e. they donate electrons and reduce other elements. They are also called as reductants or antioxidants.
- Examples: oxalic acid, ferrous sulphate, titanious sulphate, sodium thiosulphate, zinc and lithium, etc.

$KMnO_4 + FeSO_4 + H_2SO_4 \rightarrow MnSO_4 + Fe_2(SO_4)3 + K_2SO_4 + H_2O$

(Here, electrons are transferred from $FeSO_4$ to $KMnO_4$)

- Mn (+7) in $KMnO_4$ has been reduced to Mn (+2) in MnSO4.
- Fe(+2) in $FeSO_4$ has been oxidized to Fe (+3) in Fe2(SO_4)3.
- Thus, $KMnO_4$ acts as oxidizing agent and FeSO4 acts as reducing agent in acidic medium.

Half Reaction:

- In redox titrations, two reactions take place simultaneously, oxidation and reduction.

Oxidation and reduction reactions, each are known as half reactions.

Consider the following reaction:

$$Ce^{+4} + Fe^{+2} \longleftrightarrow Ce^{+3} + Fe^{+3}$$

- Oxidation half reaction may be written as:

$$Fe^{+2} \longleftrightarrow Fe^{+3} + e^{-}$$

- Reduction half reaction may be written as:

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

Detection of End Point In Redox Titrations:

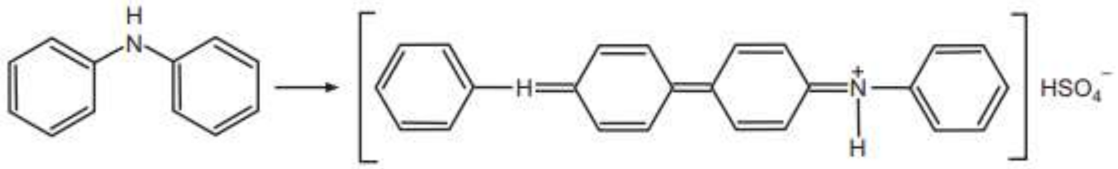
Following indicators can be used in redox titrations to determine the end point.

1. Internal or redox indicators
2. Self indicators
3. External indicators
4. Specific indicators
5. Potentiometric methods

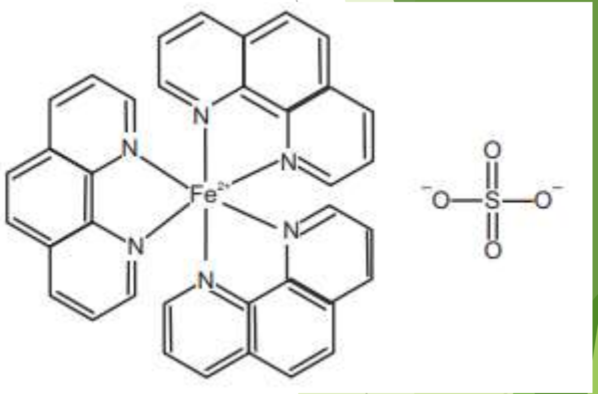
1. Internal or redox indicators : These are the redox indicators (also called an oxidation-reduction indicators) which undergo oxidation-reduction reaction at the equivalence point.

- The indicator has different colour in oxidized and reduced form. Thus, end point is marked by a colour change. There are two common types of redox indicators:
- Metal-organic complexes (Eg. phenanthroline)
- True organic redox systems (Eg. Methylene blue)

e.g. Diphenylamine



Ferroin



2. Self indicators: A coloured substance may act as its own indicator.

- For example: potassium permanganate, ceric ammonium sulphate, iodine.
- KMnO4 gets reduced in redox titration as follows:

$$MnO_4^- + 4H^+ \longleftrightarrow Mn^{2+} + 4H_2O$$

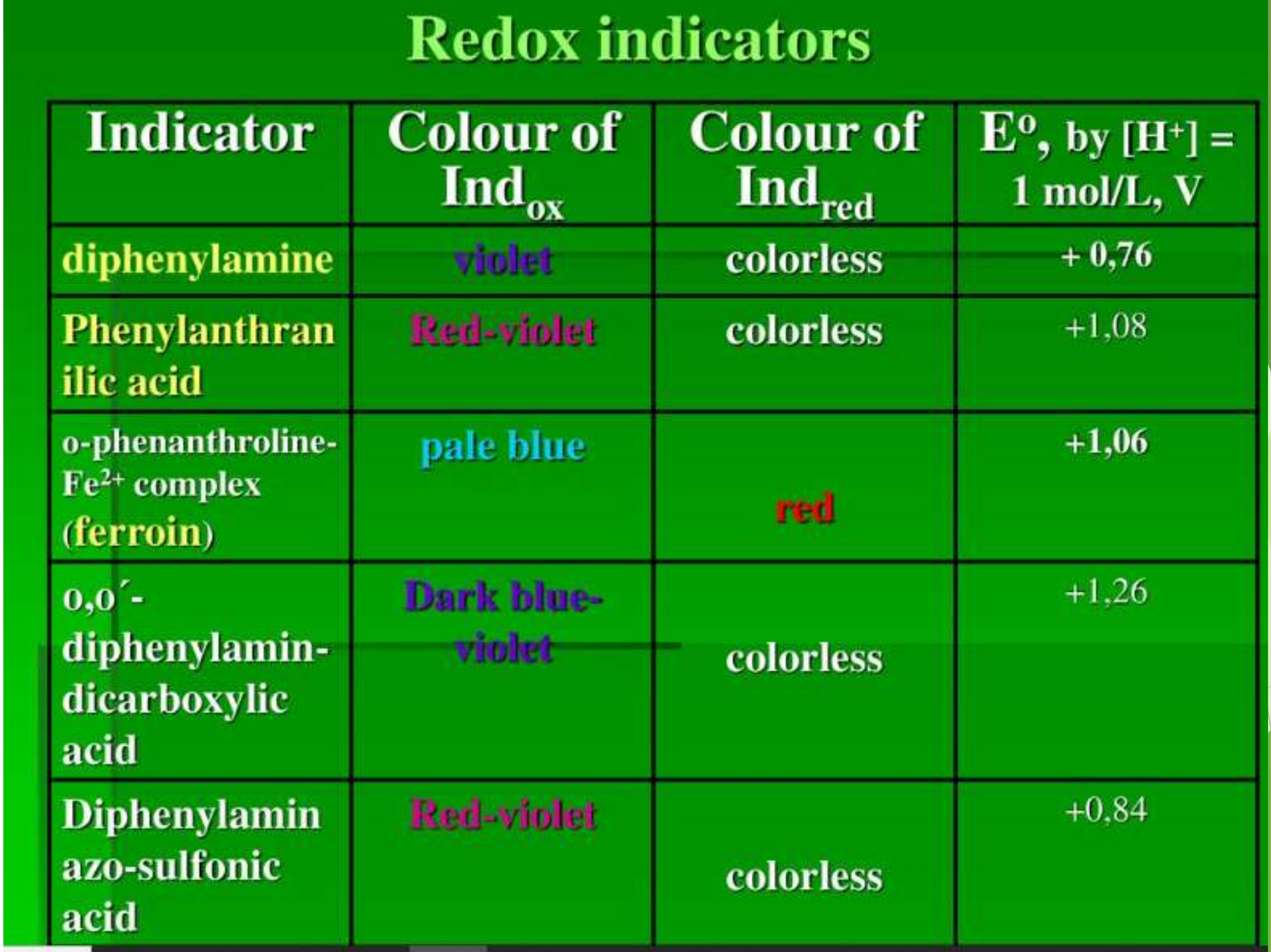
3. External indicators: These are also called as spot test indicators. These were used earlier when no indicators were available.

- For example: Ferricyanide ion was used to detect iron (II) ion by formation of iron (II) ferricyanide (Turnbull's blue) on a spot plate outside titration vessel.

4. Specific Indicators: It is as a substance which reacts in a specific manner with one of the reagents in a titration to produce colour.

- For example: Starch gives deep blue colour with iodine (1% solution of starch is used); Thiocyanate gives red colour with iron (III).

5. Potentiometric Method: It is a physicochemical method where the equivalence point is detected by large changes in potential. This method can be used when suitable indicators are not available, visual method is of limited accuracy (coloured solutions or very dilute solutions). Potential is measured by a potentiometer. At end point, there is sudden rise in potential.



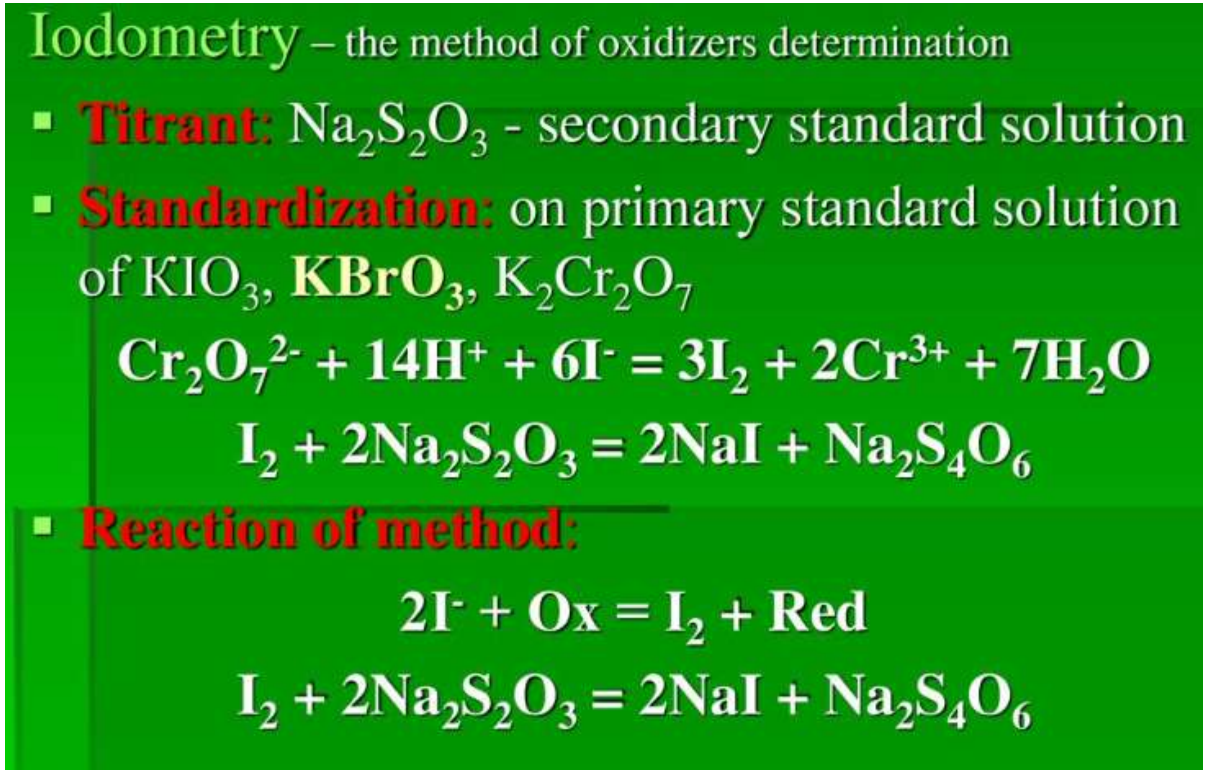
Redox indicators

Indicator	Colour of Ind$_{ox}$	Colour of Ind$_{red}$	E°, by [H$^+$] = 1 mol/L, V
diphenylamine	violet	colorless	+ 0,76
Phenylanthranilic acid	Red-violet	colorless	+1,08
o-phenanthroline-Fe^{2+} complex (ferroin)	pale blue	red	+1,06
o,o´-diphenylamin-dicarboxylic acid	Dark blue-violet	colorless	+1,26
Diphenylaminazo-sulfonic acid	Red-violet	colorless	+0,84

TYPES OF REDOX TITRATIONS

Redox titration	Titrant
Iodometry	Iodine (I_2)
Bromatometry	Bromine (Br_2)
Cerimetry	Cerium(IV) salts
Permanganometry	Potassium permanganate
Dichrometry	Potassium dichromate

1. Iodometry & Iodimetry (Iodine Titration)



Iodometry – the method of oxidizers determination

- **Titrant:** $Na_2S_2O_3$ - secondary standard solution
- **Standardization:** on primary standard solution of KIO_3, **$KBrO_3$**, $K_2Cr_2O_7$

$$Cr_2O_7^{2-} + 14H^+ + 6I^- = 3I_2 + 2Cr^{3+} + 7H_2O$$

$$I_2 + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6$$

- **Reaction of method:**

$$2I^- + Ox = I_2 + Red$$

$$I_2 + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6$$

Iodometry: The oxidizing agent oxidizes iodide to iodine. Iodine dissolves in the iodide-containing solution to give triiodide ions, which have a dark brown color. The triiodide ion solution is then titrated against standard thiosulfate solution to give iodide using starch indicator till blue colour changes to colourless.

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

$$I_2 + I^- \longrightarrow I_3^-$$

$$Na_2S_2O_3 + I_3^- \longrightarrow NaI + Na_2S_4O_6$$

I. Preparation of 0.1 M Sodium Thiosulphate Solution: Dissolve 25 g of sodium thiosulphate and 0.2 g of sodium carbonate in carbon dioxide free water and dilute to 1 litre with water.

II. Standardization of Sodium Thiosulphate: Dissolve accurately weighed 0.200 gm of **potassium bromate** in water to produce 250 ml to 50 ml of this solution. Add 2 gm of potassium iodide and 3 ml of 2M hydrochloric acid and titrate with sodium thiosulphate solution using **starch indicator** until blue colour disappears.

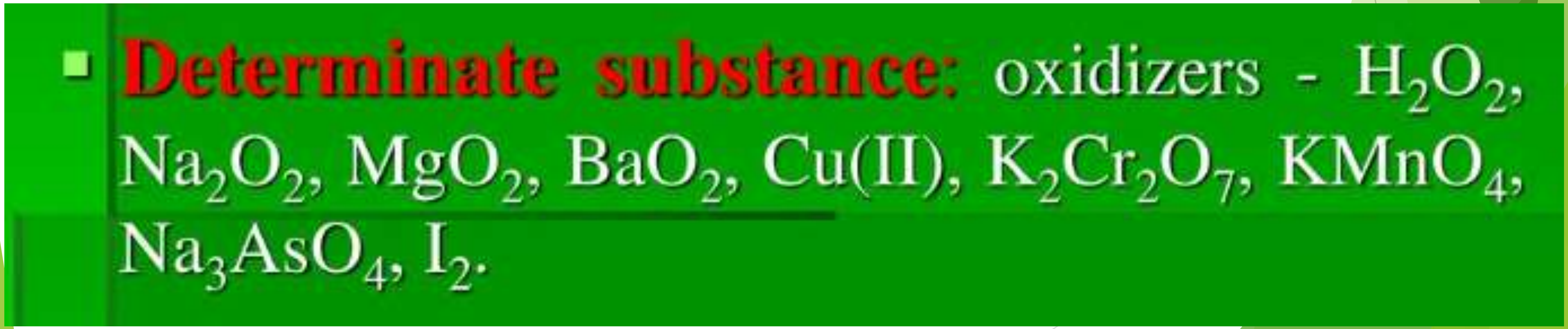
Factor: Each ml of 0.1 M sodium thiosulphate is equivalent to 0.002784 gm of KBrO3

Conditions for Iodometric Titrations:

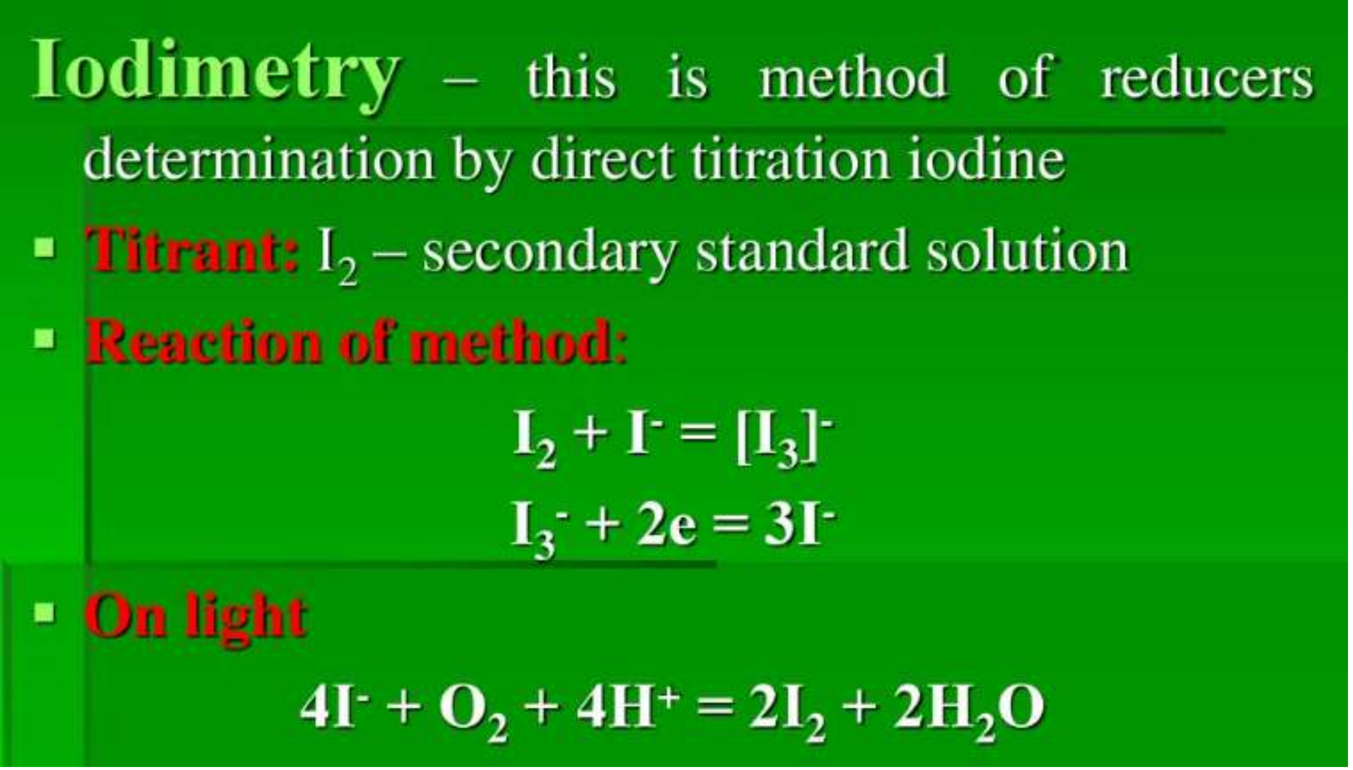
- Titration must be carried out in acidic conditions.
- In highly alkaline conditions, NaOI (Sodium hypo-iodide) is formed which is a strong oxidizing agent as compared to iodine.

$$2NaOH + I_2 \rightarrow NaOI + NaI + H_2O$$

- Reaction mixture must be kept in dark to decrease volatilization of iodine.
- Titration must be carried out in closed flask and in cold conditions to prevent volatilization of iodine.



- **Determinate substance:** oxidizers - H_2O_2, Na_2O_2, MgO_2, BaO_2, Cu(II), $K_2Cr_2O_7$, $KMnO_4$, Na_3AsO_4, I_2.



Iodimetry – this is method of reducers determination by direct titration iodine

- **Titrant:** I_2 – secondary standard solution
- **Reaction of method:**

$$I_2 + I^- = [I_3]^-$$

$$I_3^- + 2e = 3I^-$$

- **On light**

$$4I^- + O_2 + 4H^+ = 2I_2 + 2H_2O$$

Iodimetry: In iodimetry, standard solution of iodine is used as a titrant. It is based on following reaction:

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

- It is used for estimation of reducing agents like arsenates (H_3AsO_3) and thiosulphates ($Na_2S_2O_3$).

I. Preparation of Iodine Solution: Dissolve 14 gm of iodine in solution of 36 gm of potassium iodide in 100 ml of water, add 3 drops of hydrochloric acid and dilute with water to 1000 ml. Iodine is slightly soluble in water (0.00134 mol/lit). Therefore, potassium iodide is added to increase the solubility and to decrease the volatility of iodine.

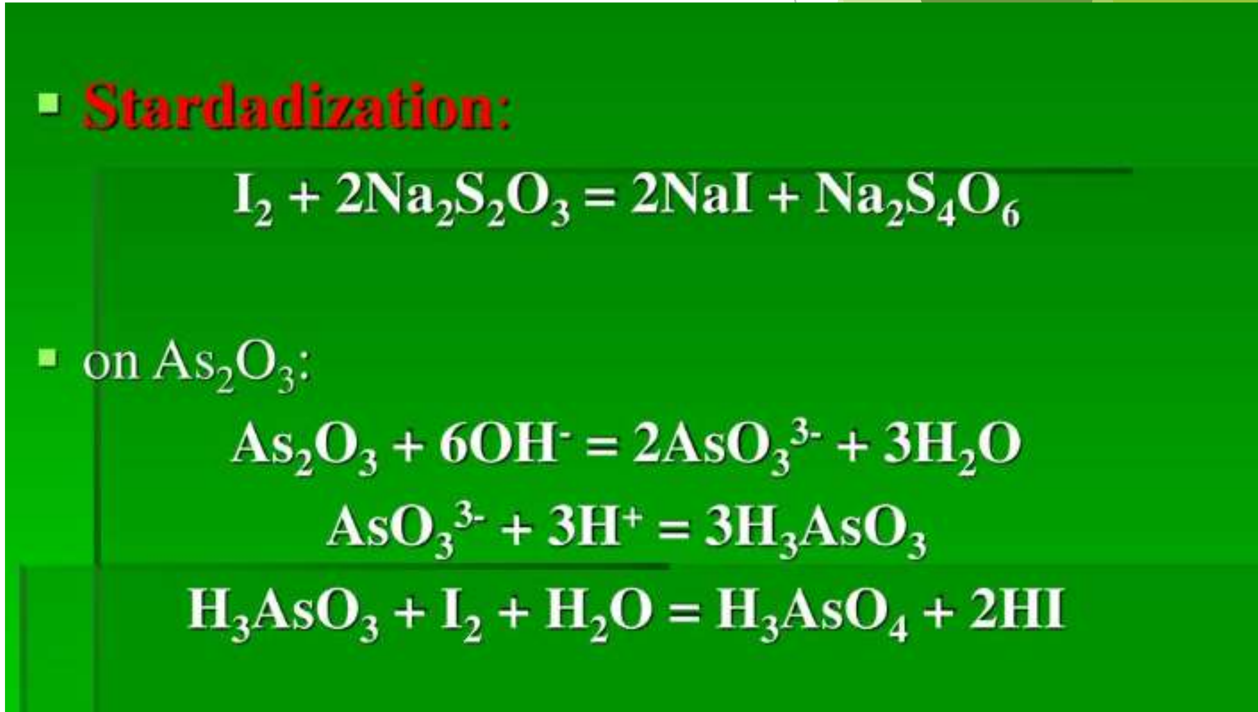
$$I_2 + I^- \longrightarrow I$$

II. a. Standardization of Iodine Solution with Arsenic Trioxide: Weigh 0.15 gm of arsenic trioxide previously dried at 105°C for 1 hour and dissolve in 20 ml of 1 M sodium hydroxide solution by warming if necessary. Dilute with 40 ml of water, add 2 drops of methyl orange solution and add dilute HCl solution until the yellow colour changes to pink. Then add 2 gm of sodium bicarbonate, dilute with 50 ml of water and add 3 ml of **starch** mucilage as indicator. Slowly titrate with iodine solution until permanent blue colour is obtained.

Conditions for Iodimetric Titrations:

1. As iodine is volatile, titration must be conducted in cold conditions.
2. As solubility of iodine is low in water, excess of KI must be used to dissolve it.
3. Sufficient time should be given before titration, as iodine ionizes too slowly.
4. The reaction mixture should be kept in dark, as light accelerates the side reactions. Iodide ions are oxidized to iodine by atmospheric oxygen.

$$4I^{-} + 4H + O_2 \rightarrow 2I_2 + 2H_2O$$



- Stardadization:

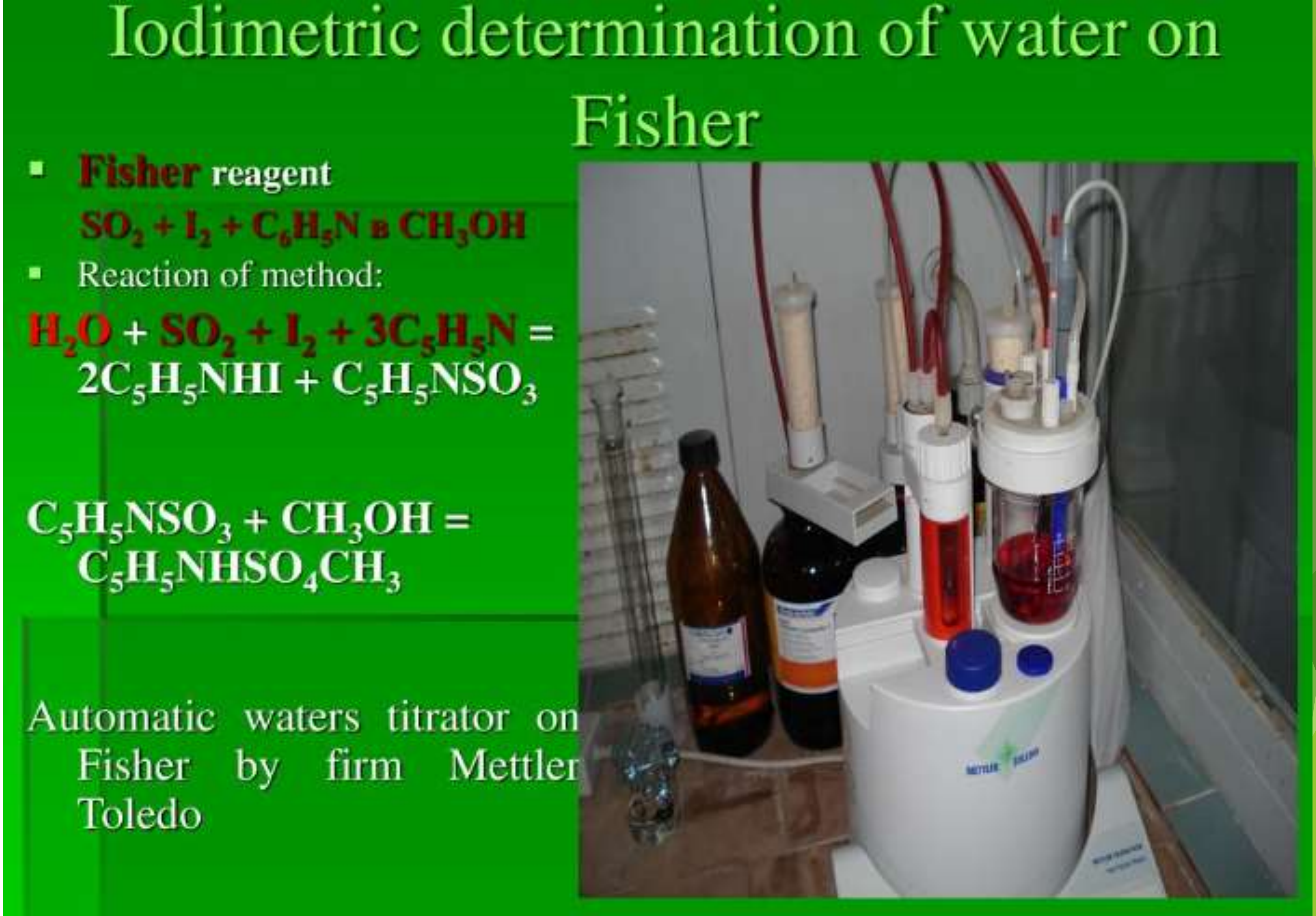
$$I_2 + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6$$

- on As_2O_3:

$$As_2O_3 + 6OH^- = 2AsO_3^{3-} + 3H_2O$$

$$AsO_3^{3-} + 3H^+ = 3H_3AsO_3$$

$$H_3AsO_3 + I_2 + H_2O = H_3AsO_4 + 2HI$$



Iodimetric determination of water on Fisher

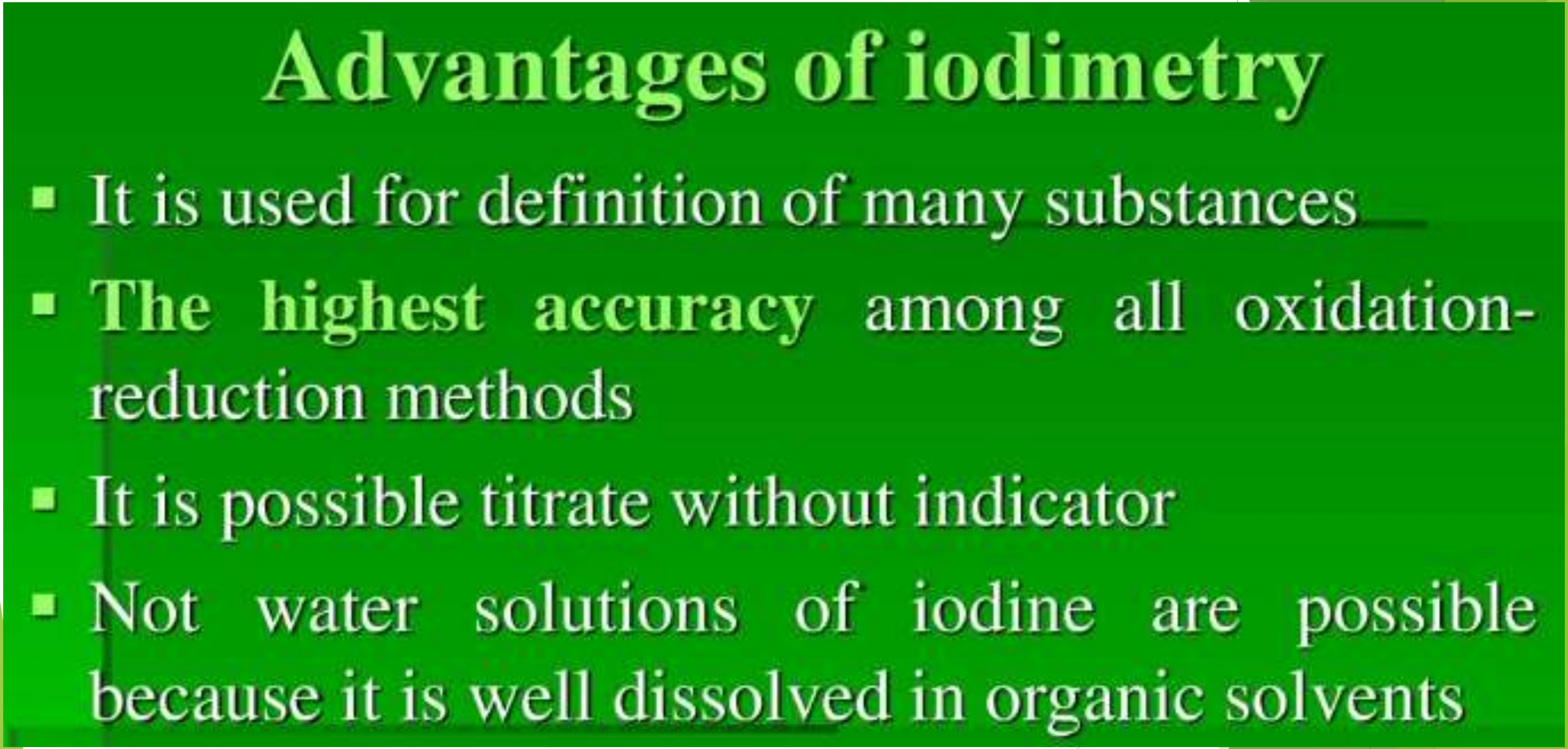
- **Fisher** **reagent**

  $SO_2 + I_2 + C_6H_5N$ в CH_3OH
- Reaction of method:

$H_2O + SO_2 + I_2 + 3C_5H_5N =$
$2C_5H_5NHI + C_5H_5NSO_3$

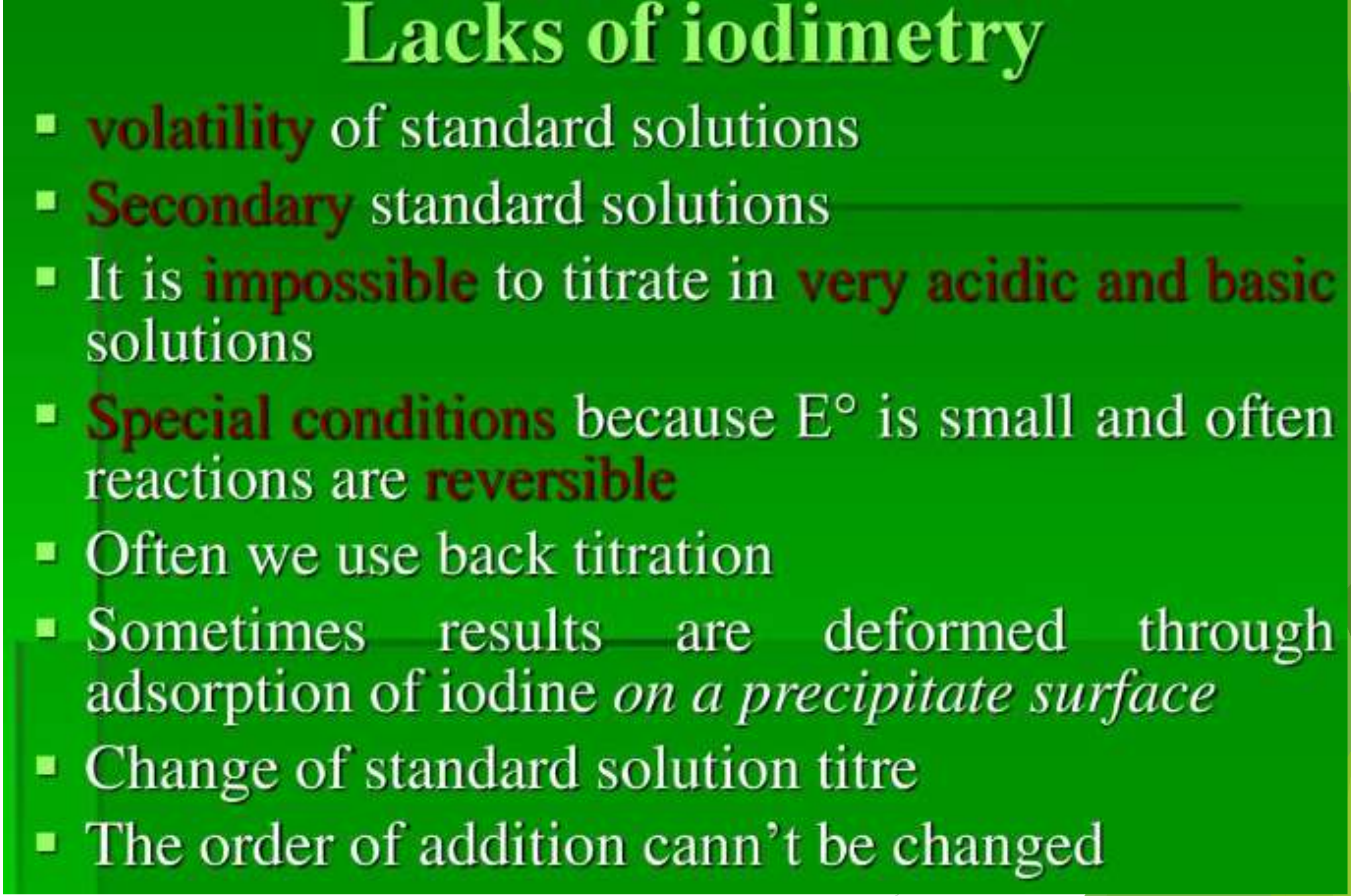
$C_5H_5NSO_3 + CH_3OH =$
$C_5H_5NHSO_4CH_3$

Automatic waters titrator on Fisher by firm Mettler Toledo



Advantages of iodimetry

- It is used for definition of many substances
- **The highest accuracy** among all oxidation-reduction methods
- It is possible titrate without indicator
- Not water solutions of iodine are possible because it is well dissolved in organic solvents



Lacks of iodimetry

- **volatility** of standard solutions
- **Secondary** standard solutions
- It is **impossible** to titrate in **very acidic and basic** solutions
- **Special conditions** because E° is small and often reactions are **reversible**
- Often we use back titration
- Sometimes results are deformed through adsorption of iodine *on a precipitate surface*
- Change of standard solution titre
- The order of addition cann’t be changed

2. Bromatometry

- **When potassium bromates (KBrO3) is used as titrant, the titration is known as Bromatometry.**
- Potassium bromate is a strong oxidizing agent and is used for assay of number of pharmaceutical substances like, mephensin, phenol, sodium salicylate, etc.
- Reagent can be employed in 2 ways:

1. Direct titration
2. Bromination

1. Direct titration: Reducing substances like As (III), Sb (II), Fe (II) and certain organic sulphides and disulphides can be titrated directly with potassium bromate.

$$\mathbf{BrO_3^- + HAsO_2 \rightarrow Br^- + HAsO_3}$$

$$\mathbf{BrO_3^- + Br^- + H+ \rightarrow Br_2 + H_2O}$$

- Appearance of bromine is sometimes suitable for detection of end point. Organic indicators like alpha-naphthoflavone, quinoline yellow and p-ethoxychrysoidine can also be used.

2. Bromination of Organic Compounds: Potassium bromate-potassium bromide (KBr-$KBrO_3$) mixture is used for liberation of bromine.

$$KBrO_3 + 5KBr + 3H_2SO_4 \rightarrow 3K_2SO_4 + 3Br_2 + 3H_2O$$

- Bromine is then used for bromination of organic compounds. Excess of Bromine is then determined by addition of KI.

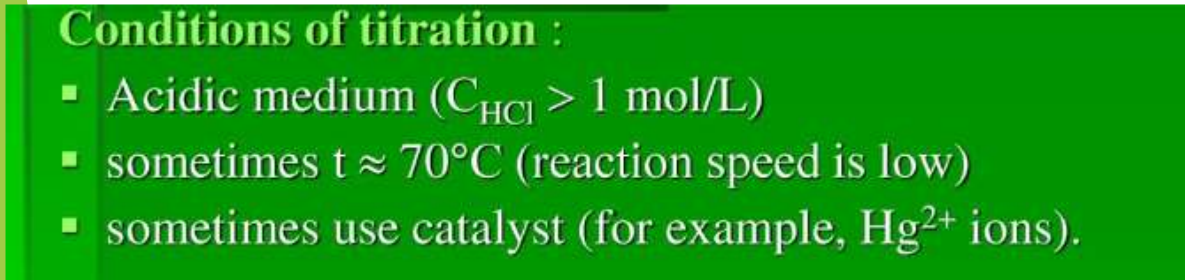
$$Br_2 + KI \rightarrow I_2 + Br^-$$

$$I2 + S_2O_3{}^{2-} \rightarrow I^- + S_4O_6{}^{2-}$$

I. Preparation of 0.1 N Potassium Bromate: Weigh accurately about 2.784 gm of potassium bromate and 12 gm of potassium bromide in water and dilute to 1000 ml with water.

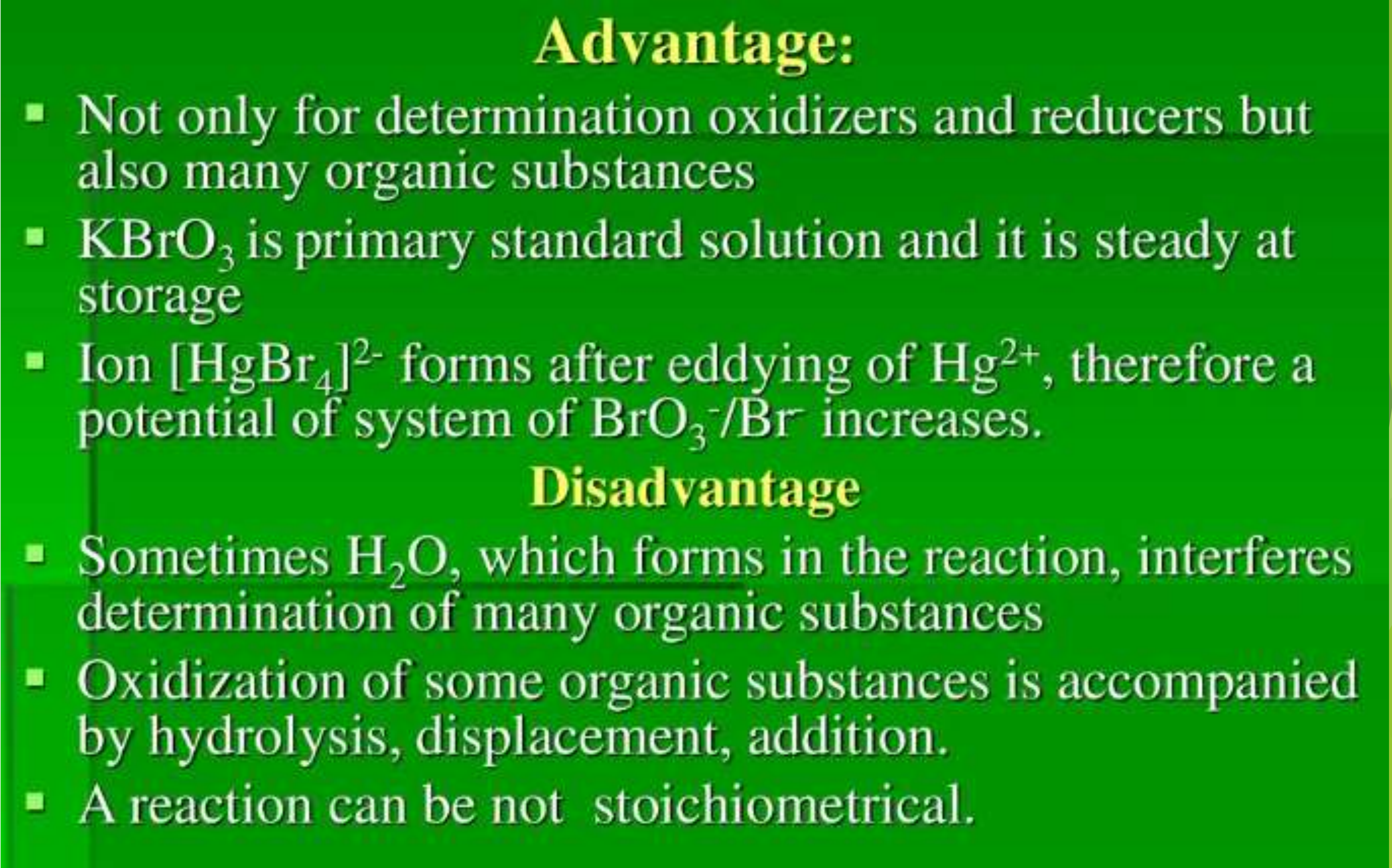
II. Standardization of Potassium Bromate: Transfer 30 ml of 0.1 N potassium bromate solution in 250 ml iodine flask. Add 3 gm potassium iodide and 3 ml of hydrochloric acid. Mix the contents thoroughly and allow to stand for 5 minutes. Titrate the liberated iodine with previously standardized 0.1 N sodium thiosulphate using 3 ml of freshly prepared **starch solution** as indicator added towards the end.

Factor: Each ml of 0.1 N sodium thiosulphate is equivalent to 0.002784 gm of $KBrO_3$.



Conditions of titration :

- Acidic medium ($C_{HCl} > 1$ mol/L)
- sometimes t ≈ 70°C (reaction speed is low)
- sometimes use catalyst (for example, Hg^{2+} ions).



Advantage:

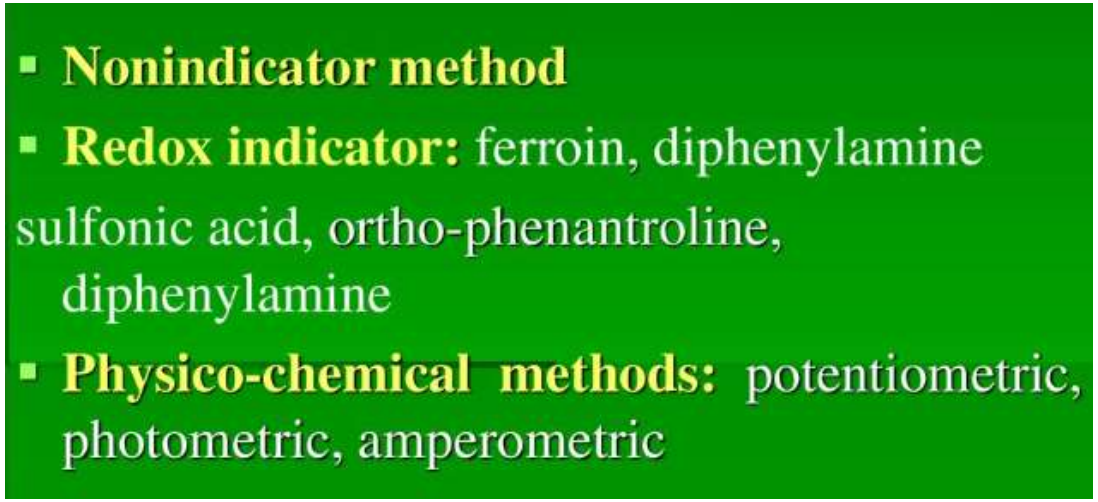
- Not only for determination oxidizers and reducers but also many organic substances
- $KBrO_3$ is primary standard solution and it is steady at storage
- Ion $[HgBr_4]^{2-}$ forms after eddying of Hg^{2+}, therefore a potential of system of BrO_3^-/Br^- increases.

Disadvantage

- Sometimes H_2O, which forms in the reaction, interferes determination of many organic substances
- Oxidization of some organic substances is accompanied by hydrolysis, displacement, addition.
- A reaction can be not stoichiometrical.

3. Cerimetry

- **Titrations involving determinations with cerium compounds are called Cerimetry.**
- Atomic weight of Cerium is 140 gm/mol.
- It exists in 2 oxidation states: +4 and +3.
- In tetravalent (Quadrivalent) state it acts as a powerful oxidizing agent.
- It is of dark yellow colour in concentrated solution.
- On reduction trivalent cerium ion is obtained, which is colourless.
- Some of the compounds of Cerium such as Ceric ammonium nitrate $(NH_4)2Ce(NO_3)6$, Ceric ammonium sulphate $(NH_4)4Ce(SO_4)4$, Ceric hydroxide Ce(OH)4 can be used for determination.
- Indicators:



- **Nonindicator method**
- **Redox indicator:** ferroin, diphenylamine sulfonic acid, ortho-phenantroline, diphenylamine
- **Physico-chemical methods:** potentiometric, photometric, amperometric

I. **Preparation of 0.1 M Ceric Ammonium Nitrate Solution:** Dissolve 65 gm of ceric ammonium sulphate with help of gentle heat, in a mixture of 30 ml sulphuric acid and 500 ml water. Cool it. Filter if turbid and dilute with water to 1000 ml.

II. **Standardization of 0.1 M Ceric Ammonium Nitrate Solution:** Weigh accurately about 0.2 gm of arsenic trioxide, previously dried at 105°C for 1 hour and transfer to 500 ml conical flask. Wash with 25 ml of 8% w/v solution of sodium hyrdroxide, 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 ceric ammonium nitrate, until pink colour is changed to very pale blue.

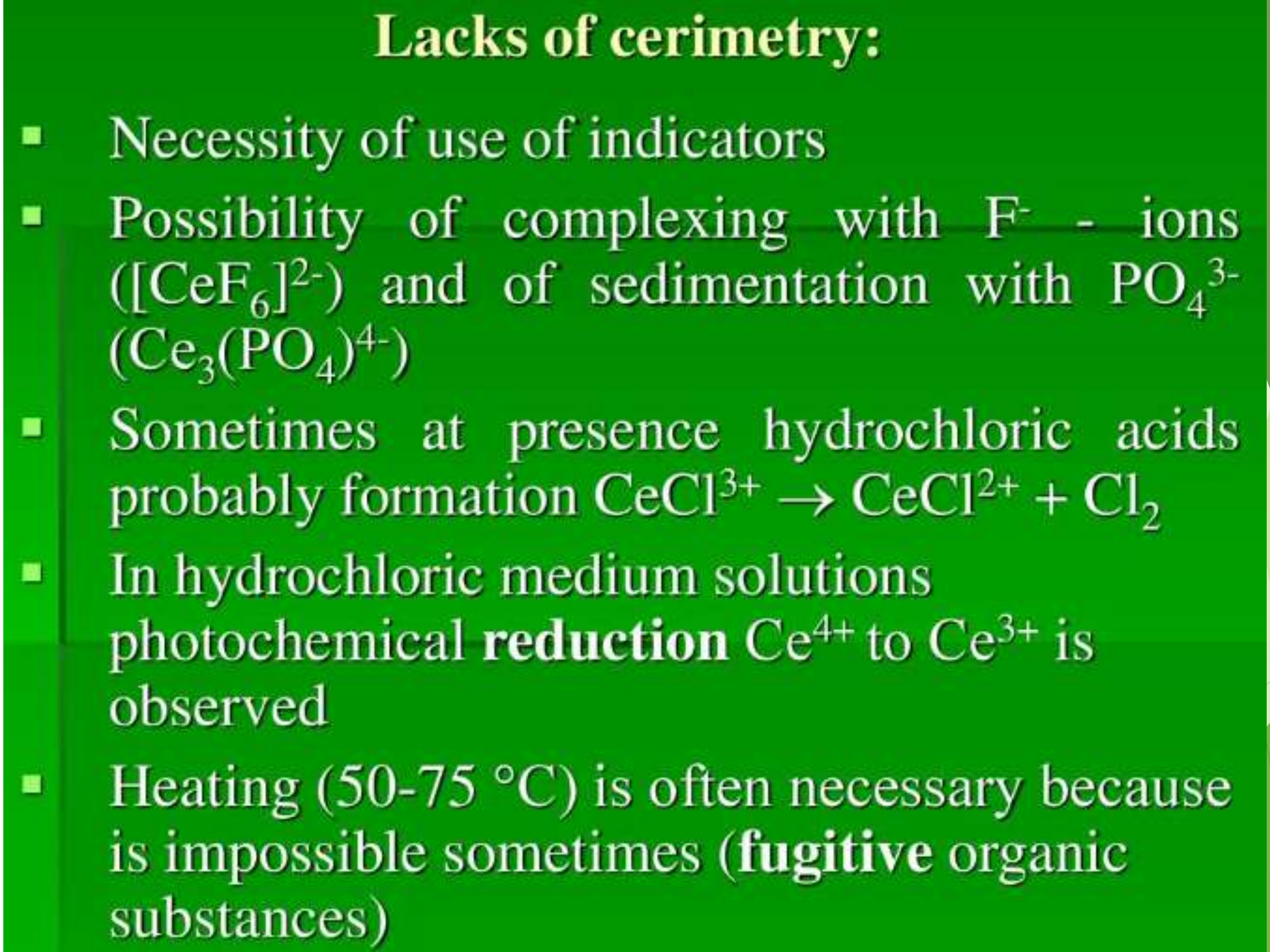
Factor: Each ml of 0.1 M ceric ammonium nitrate is equivalent to 0.004946 gm of As_2O_3.

Advantages of Cerimetry over Pemanganometry:

- Cerium can be reduced to only one oxidation state.
- It is very strong oxidizing agent and its intensity can be varied using different acids.
- Sulfuric acid solutions are extremely stable.
- No effect of light or heating for short time.
- Cerium nitrate is available in sufficiently pure form to directly prepare standard solution.

Applications of Cerimetry:

- Titration of hydrogen peroxide.
- Ferrous compounds can be analyzed.
- Oxalates can be analyzed using ceric sulphate.
- Analysis of tartaric acid, phthalic acid, saliculic acid.
- Nitrogen compounds like hydroxylamines, nitrites can also be analyzed.



Lacks of cerimetry:

- Necessity of use of indicators
- Possibility of complexing with F^- - ions ($[CeF_6]^{2-}$) and of sedimentation with PO_4^{3-} ($Ce_3(PO_4)^{4-}$)
- Sometimes at presence hydrochloric acids probably formation $CeCl^{3+} \rightarrow CeCl^{2+} + Cl_2$
- In hydrochloric medium solutions photochemical **reduction** Ce^{4+} to Ce^{3+} is observed
- Heating (50-75 °C) is often necessary because is impossible sometimes (**fugitive** organic substances)

4.Permagnometry

- Potassium permanganate is widely used as oxidizing agent in redox titrations.
- It is readily available and inexpensive. It requires no indicators except in very dilute solutions.
- Permanganate undergoes a variety of chemical reactions, since manganese can exist in oxidation states of +2, +3, +4, +6, +7.
- It reacts rapidly with reducing agents as follows:

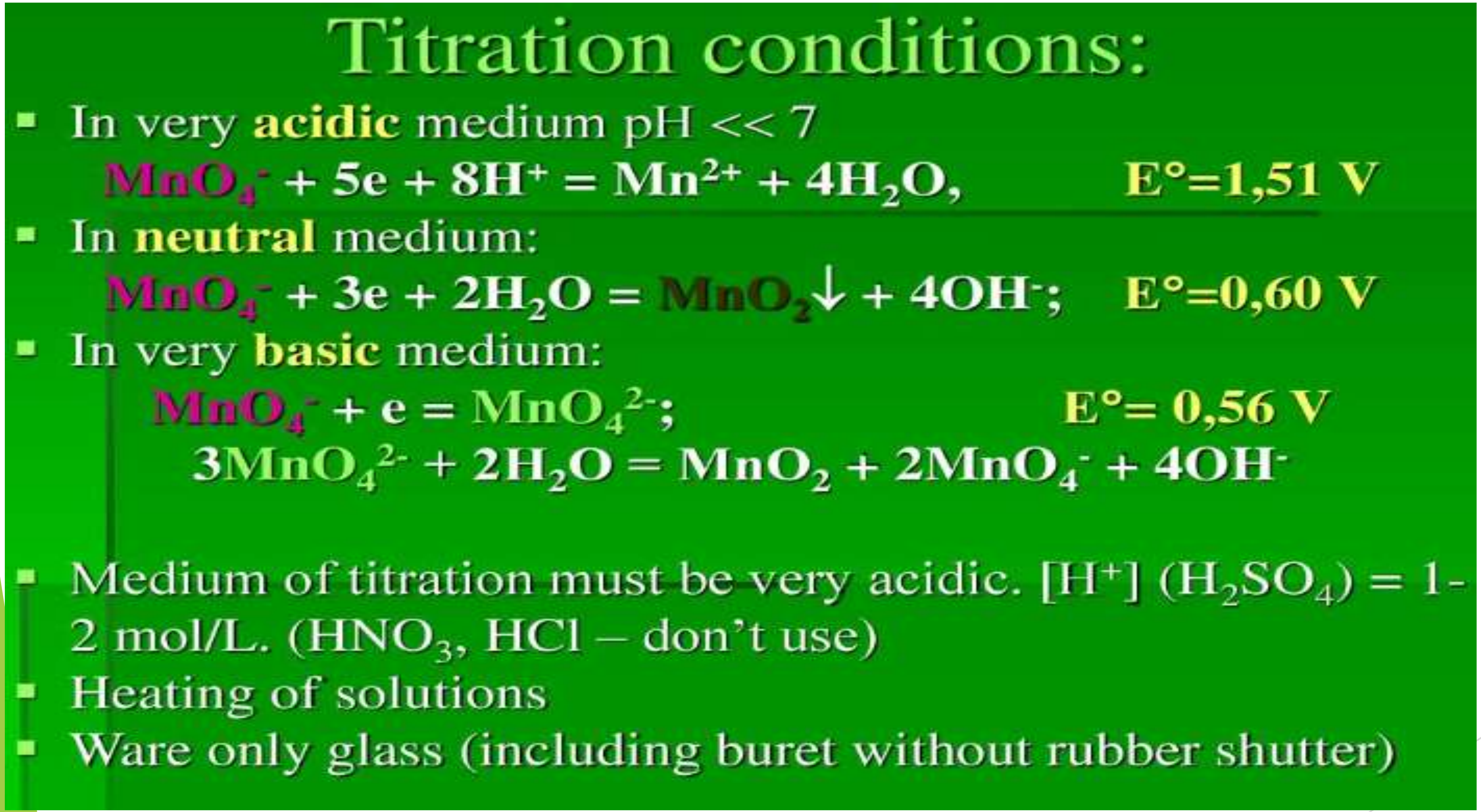
$$\mathbf{MnO_4^- + 8H^+ + 5e^- = Mn^{+2} + 4H_2O}$$

I. Preparation of 1 M KMnO4: Dissolve 158 gm of KMnO4 in water to make up volume to 1000 ml. Heat on water bath for 1 hour, allow standing for 2 days. Filter through glass wool.

II. a) Standardization of KMnO4: Primary standards like Arsenious oxide, Sodium oxalate/Oxalic acid, Sodium thiosulphate, Iron can be used for standardization of potassium permanganate.

II. b) Standardization with Sodium Oxalate: Dissolve 6.7 gm of sodium oxalate previously dried at 110°C in water and then make up volume to 1 litre. Pipette out 20 ml of this solution to conical flask, add 5 ml of concentrated sulphuric acid and then warm to 70°C. Titrate against KMnO4 until pink colour persists for 30 s.

$$5Na_2C_2O_4 + 2KMnO_4 + 8H_2SO_4 \longrightarrow K_2SO4 + 2MnSO_4 + 10CO_2 + 5Na_2SO_4 + 8H_2O$$



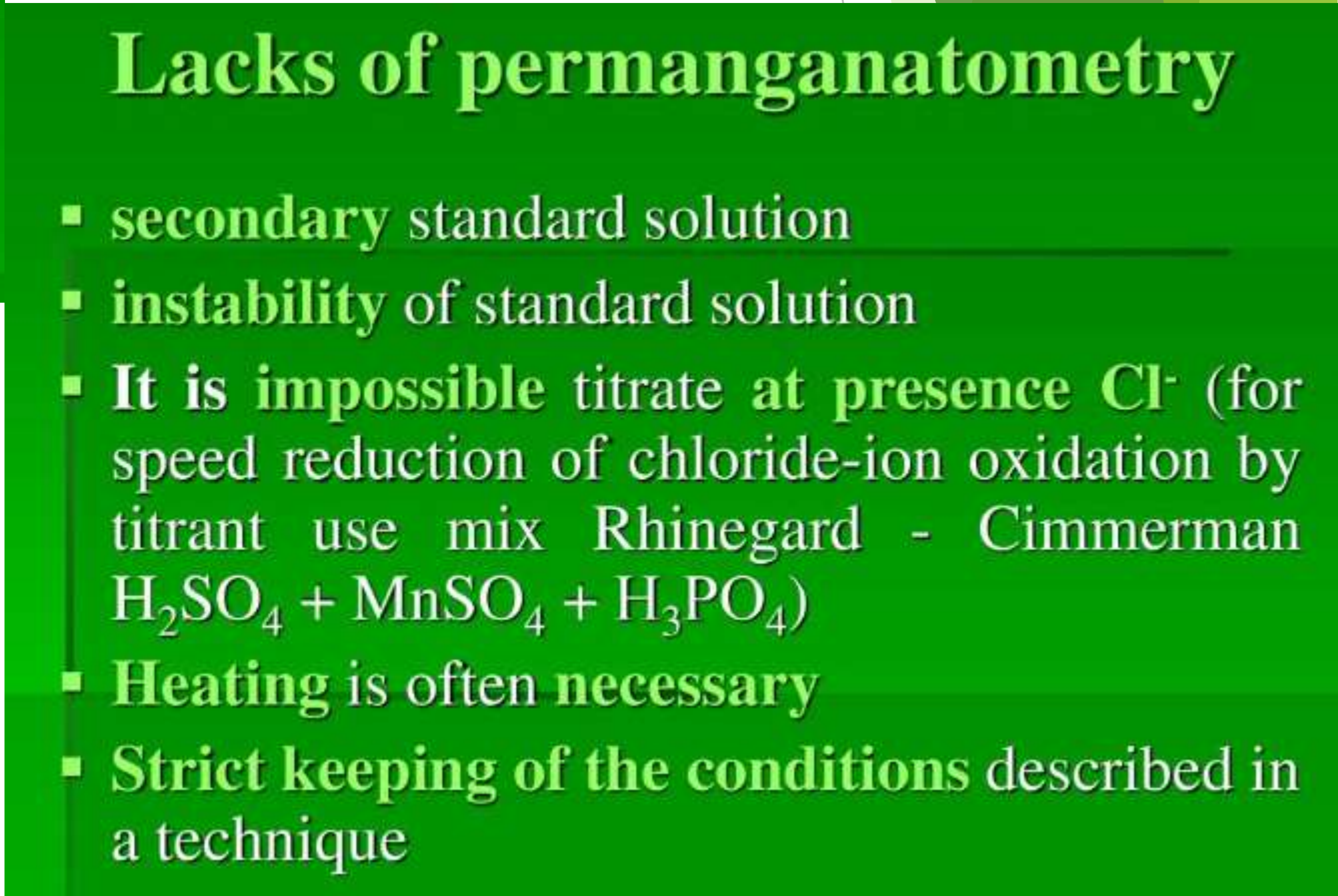
Titration conditions:

- In very **acidic** medium pH << 7
  $MnO_4^- + 5e + 8H^+ = Mn^{2+} + 4H_2O,$ $E° = 1,51$ V
- In **neutral** medium:
  $MnO_4^- + 3e + 2H_2O = MnO_2\downarrow + 4OH^-;$ $E° = 0,60$ V
- In very **basic** medium:
  $MnO_4^- + e = MnO_4^{2-};$ $E° = 0,56$ V
  $3MnO_4^{2-} + 2H_2O = MnO_2 + 2MnO_4^- + 4OH^-$

- Medium of titration must be very acidic. $[H^+]$ $(H_2SO_4) = 1-2$ mol/L. (HNO_3, HCl – don't use)
- Heating of solutions
- Ware only glass (including buret without rubber shutter)

Advantages of permanganatometry

- Titration without indicator
- Possibility of use of a wide interval of pH
- High value of E°
- Cheap and accessible reagent
- Possibility of definition of substances which haven’t oxidation-reduction properties



Lacks of permanganatometry

- **secondary** standard solution
- **instability** of standard solution
- **It is impossible** titrate **at presence** Cl^- (for speed reduction of chloride-ion oxidation by titrant use mix Rhinegard - Cimmerman $H_2SO_4 + MnSO_4 + H_3PO_4$)
- **Heating** is often **necessary**
- **Strict keeping of the conditions** described in a technique

5.Dichrometry

- Titration involving potassium dichromate ($K_2Cr_2O_7$) as titrant is known as dichrometry. Dichromate titrations are based on conversion of dichromate ion containing hexavalent chromium into trivalent chromium ions.

$$Cr_2O^{2-}_7 + 14\,H^{+} + 6e \rightarrow 2Cr^{+3} + 7H_2O$$

- **Indicators:**

External indicators: Potassium ferricyanide.

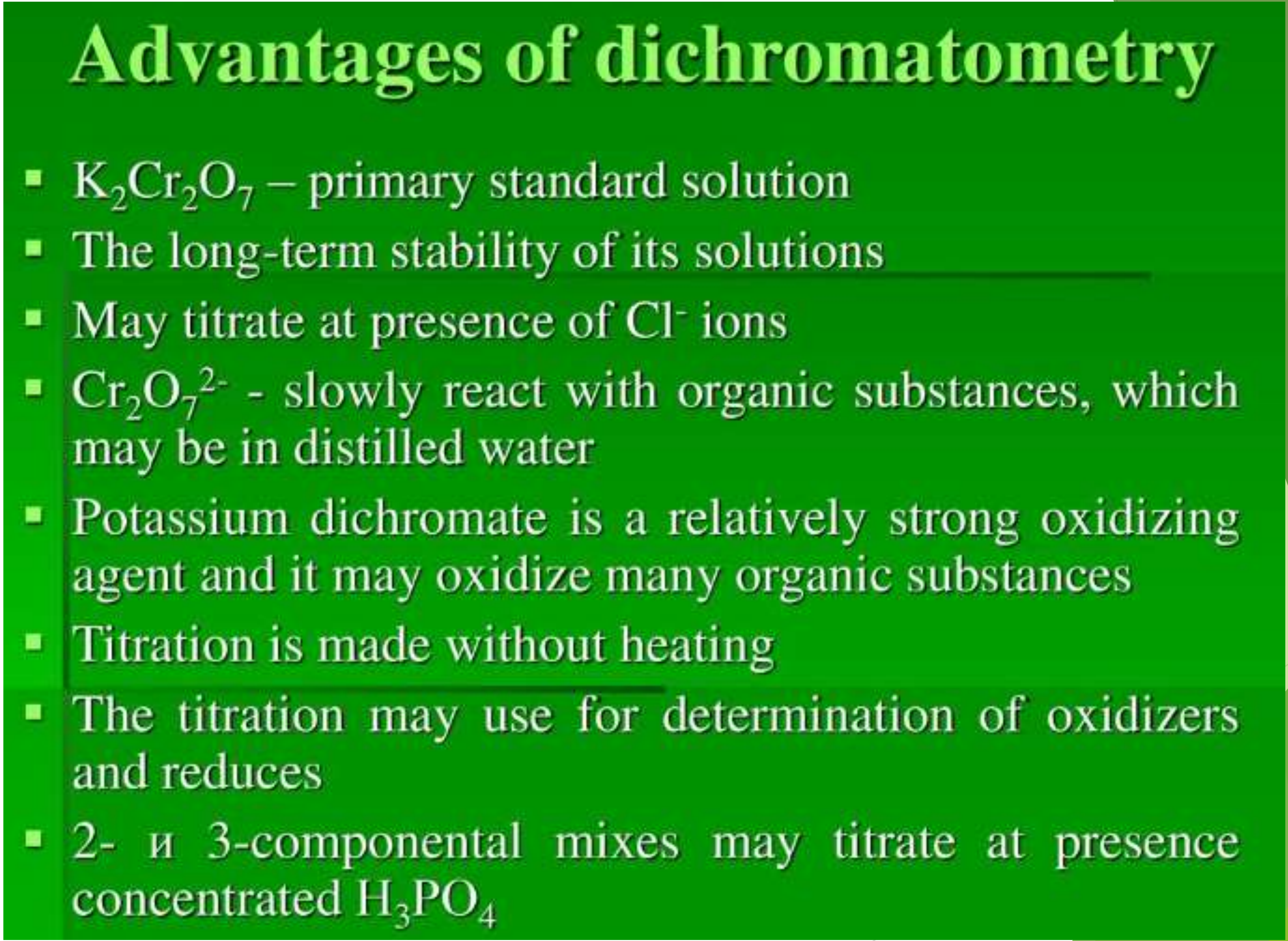
Internal indicators: Diphenylamine, Diphenylbenzidine, Diphenylamine sulfonate.

Colour change: green to violet

I. Preparation of 0.1 N K2Cr2O7: Dissolve 4.9036 gm equivalent of $K_2Cr_2O_7$ previously powdered and dried in a dessicator for 4 hours, and dissolve in water to produce 1000 ml. Potassium dichromate can be obtained as a primary standard reagent and standard solution may be prepared determinately and stored for long periods of time.

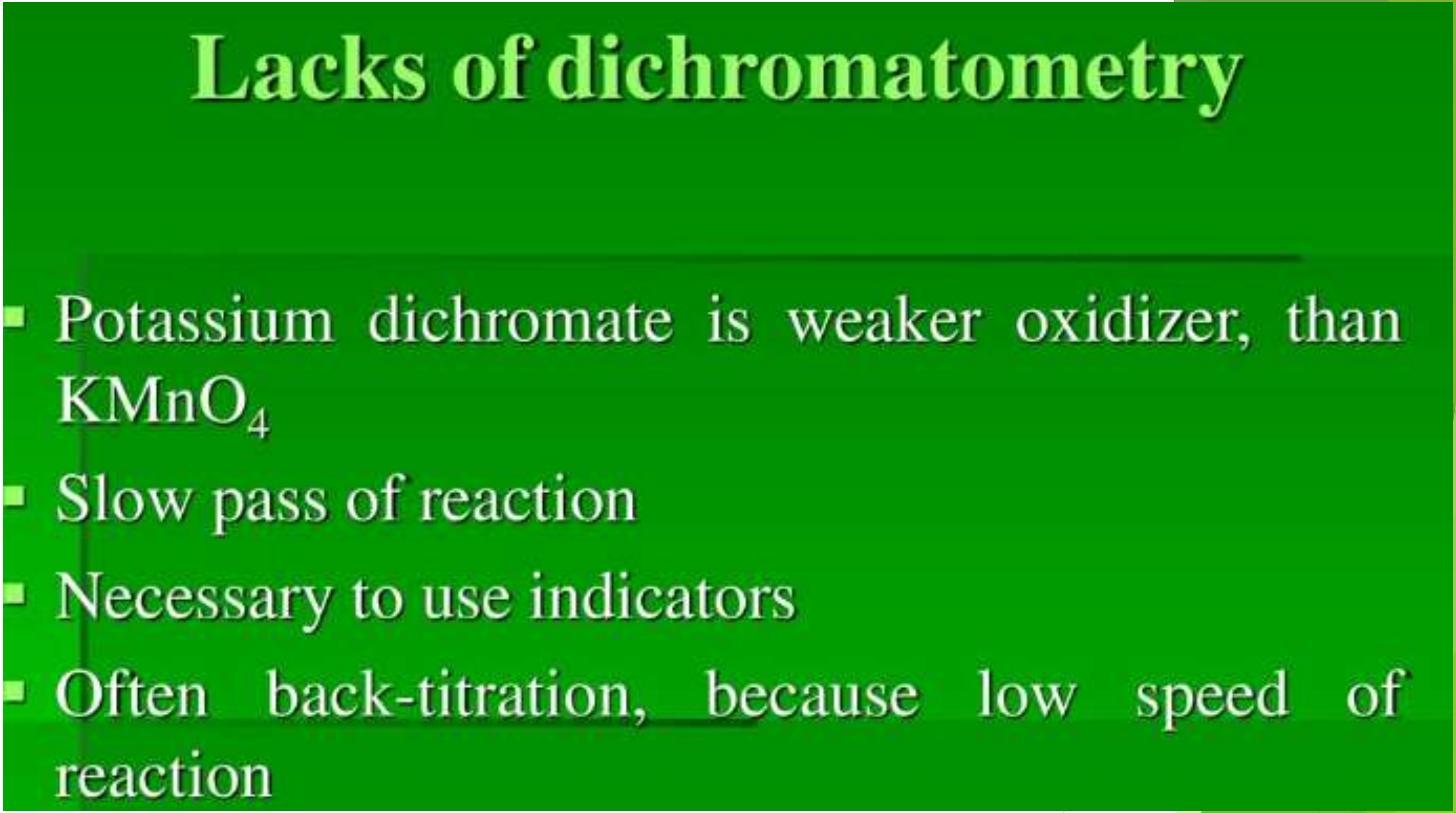
II. Standardization of Potassium Dichromate: To 20 ml of solution, add 1 gm of potassium iodide and 7 ml of 2 M hydrochloric acid. Add 250 ml water and titrate against 0.1 m sodium thiosulphate using 3 ml starch solution until the colour changes from blue to light green.

Factor: Each ml of sodium thiosulphate is equivalent to 0.0049 gm of $K_2Cr_2O_7$.



Advantages of dichromatometry

- $K_2Cr_2O_7$ – primary standard solution
- The long-term stability of its solutions
- May titrate at presence of Cl^- ions
- $Cr_2O_7^{2-}$ - slowly react with organic substances, which may be in distilled water
- Potassium dichromate is a relatively strong oxidizing agent and it may oxidize many organic substances
- Titration is made without heating
- The titration may use for determination of oxidizers and reduces
- 2- и 3-componental mixes may titrate at presence concentrated H_3PO_4



Lacks of dichromatometry

- Potassium dichromate is weaker oxidizer, than $KMnO_4$
- Slow pass of reaction
- Necessary to use indicators
- Often back-titration, because low speed of reaction

Question Bank

Short Answer Questions:

1. What are redox titrations?
2. Enlist the various titrants used in redox titrations.
3. Name redox indicators.
4. What is iodimetry?
5. What is equivalent weight?
6. Explain equivalent weights concept.
7. Explain the Nernst equation.
8. What are conditions for iodometric titrations.
9. Give difference between iodometry and iodimetry.
10. How will you prepare and standardize 0.1 N sodium thiosulphate.
11. How will you prepare and standardize 0.1 M ceric ammonium nitrate.
12. How will you prepare and standardize 0.1 N Iodine solution.
13. Explain the titrations with potassium iodate.

Long Answer Questions:

1. Explain the concepts of oxidizing agent and reducing agent in redox titrations.
2. Explain the methods to balance redox reactions.
3. Explain the methods of end point detection in redox titrations.
4. Write a note on permanganometry.
5. Write a note ion cerimetry.
6. Give an account of dichrometry.
7. Write a note on bromatometry.
8. Write a note on preparations of potassium permanganate. What precautions are to be kept while preparing it.

Thank You…