SHREE H. N. SHUKLA INSTITUTE OF PHARMACEUTICAL EDUCATION AND RESEARCH

B.PHARM

(SEMESTER –I)

SUBJECT NAME: PHARMACEUTICAL ANALYSIS -I

SUBJECT CODE: BP102TP

UNIT 4: REDOX TITRATIONS

Content

Redox titrations:
(a) Concepts of oxidation and reduction
(b) Types of redox titrations (Principles and applications)
Cerimetry, Iodimetry, Iodometry, Bromatometry, Dichrometry, Titration with potassium iodate

INTRODUCTION

Concept of oxidation and reduction

As discussed before, in titrimetric analysis we can find out the quantity of pure component based on measurement of volume of standard solution that reacts completely with the analyte.

This measurement of standard solution can be possible in different reactions, and if the reaction involved in this measurement is oxidation-reduction reaction, that method is called as "oxidation reduction titration" or "Redox titration.
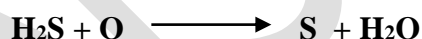
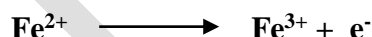In Redox titration oxidation & Reduction reaction occurs simultaneously.

Oxidation

Combination of the substance with oxygen is termed as oxidation.

$$C_{(s)} + O_{2\,(g)} \longrightarrow CO_{2\,(g)}$$
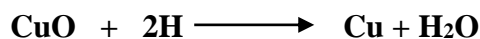
Removal of Hydrogen

$$H_2S + O \longrightarrow S + H_2O$$

Loss of electron(s) is known as oxidation. By loosing electron positive valency of element increases and negative valency of element decreases.
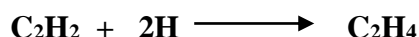
$$Fe^{2+} \longrightarrow Fe^{3+} + e^-$$

Increase in oxidation number

Reduction

Removal of Oxygen from substance

$$CuO + 2H \longrightarrow Cu + H_2O$$

Additon of Hydrogen

$$C_2H_2 + 2H \longrightarrow C_2H_4$$

Gain of electron, by taking on electron positive valency is decreased and negative valency is increased.

$$Fe^{3+} + e^- \longrightarrow Fe^{2+}$$
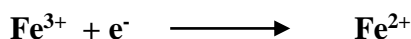
Decrease in Oxidation number.

Oxidation-Reduction Reaction

*   Oxidation-reduction reactions are the chemical processes in which a change in the valency of reacting elements or ions takes place.

*   The valency of an element represents the number of electrons which it atoms take on or give up on reacting with other elements to form the compound.

*   Depending on the compound in which element is available, the valency of some elements varies e.g. Iron can be bivalent or trivalent (in $FeCl_2$, $FeCl_3$, respectively), the manganese can have valencies from 2 to 7 (MnO, MnO_2, Mn_2O_3, Mn_2O_7).

*   Oxidation-reduction reaction is thus a process involving the transfer of electrons from one element or ion to another resulting in the change of the valency of reacting atoms or ions.

*   **Oxidizing agents** oxidizes reducing agent by accepting their electron and itself get reduced, whereas **Reducing agent** reduces oxidizing agent by giving up their electron and itself get oxidised .

$$\text{(oxidized)} \quad \text{(Reduced)}$$

$$Fe^{2+} \quad + \quad Ce^{4+} \longrightarrow Fe^{3+} + Ce^{3+}$$

(Reducing agent)   (Oxidizing agent)
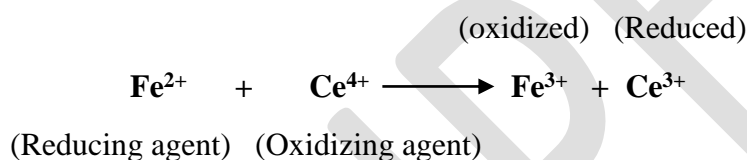
Oxidation State/Oxidation Number

Oxidation number is positive /zero/negative integer.

Comparative +ve oxidation State (O.S) reflects LEO and –ve OS reflects GER.

$$K \longrightarrow +1 \qquad NaCl \longrightarrow 0 \qquad Cl \longrightarrow -1$$

Rules for assigning oxidation state

The sum of the OS of all the atoms in a molecule/ion must be equal in sign and value to the charge on that molecule or ion.

$$H_2SO_4 \longrightarrow 2H^+ \quad + \quad SO_4^{2-} \quad \{S \longrightarrow +6, O \longrightarrow 4 (-2) = -8\}$$

(zero)   2 X (+1)   (-2)
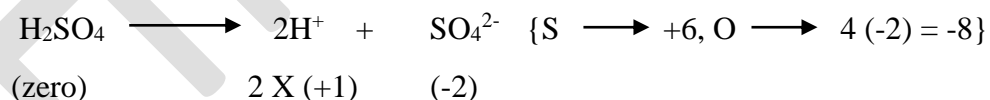
Certain elements assume the same oxidation state in different compounds.

Halogens (F, Cl Br, I) = -1

Alkali Metals (Li, Na, K) = +1

Alkali earth metals (ca, Mg, Ba, Be, Sr, Ra) = +2

Oxgen is having -2 OS in general. But if in the form of Hydrogen peroxide oxygen has -1 OS.

Many elements (specially nonmetals) can assume a variety of oxidation state.

For e.g. NH_3 = **X** x (+1)x 3 = 0 HNO_3 = +1 x **X** x (-2)x 3 = 0

        X = -3   **X** = +5

Half Reactions:

- As seen in acid-base reactions, an acid is defined as proton donor and a base as a proton acceptor.

- The acid-base properties of a conjugate pair are not possible in absence of a second conjugate pair, Acid-base reaction is thus a transfer of a proton from one conjugate pair to another.

- The redox reactions have similar situations. In these reactions also two half reactions must be involved, each half reaction includes a redox conjugate pair and the net result of redox reaction will be transfer of one or more electrons from one pair to the other. General redox half reaction can be written as –

oxidation

**Reducing agent $\longrightarrow$ Oxidizing agent**

Reduction
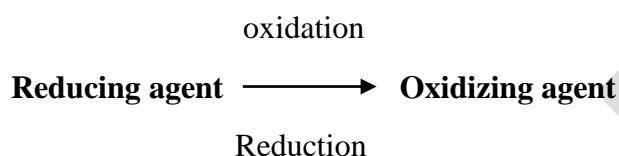
- In other words, it is not possible to observe a redox half reaction. Two half redox reactions are required, one to liberate electrons and one to accept it.

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

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

$$H_2 \longrightarrow 2H^+ + 2e$$
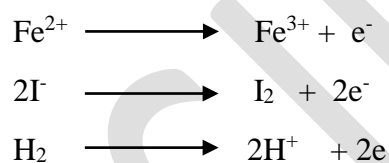
REDOX POTENTIAL

- It can be calculated by measuring the potential difference of a cell in which oxidation reduction half cell is coupled with standard reference cell, i.e. standard hydrogen electrode.

- Oxidising agents gain electrons and get reduced while reducing agents lose electrons and get oxidised.

- This transfer of electrons leads to the changes in the valency of the atoms or ions. The positive valency of oxidised atom or ion is increased while that of reduced atom or ion is decreased. Oxidising and reducing agents may differ in strength i.e. chemical activity.

- Strong oxidising agents have a pronounced tendency to accept/gain electrons and hence, they are having ability to take up the electrons from many reducing agents even relatively weak one.

- Weak oxidising agents have a much less pronounced tendency to gain electrons i.e. they can oxidise only strong reducing agents.

- The direction of a redox reaction can be predicted provided some quantitative characteristic of the relative force involved is known. This characteristic is known as the 'Redox Potential.

- It is possible to measure the potential difference between two systems by connecting them into a galvanic cell.

- Any galvanic element consists of two half elements. Each of which is oxidation-reduction couple i.e. a system consisting of the oxidised and the reduced form of the chemical element or ion.

- The more powerful the oxidant of the pair, the weaker its reductant should be and vice versa; if Cl_2, is said to be a powerful oxidising agent, this means its atoms possess the pronounced ability to accept electrons, changing to Cl^-. In other words, Cl^- should keep a strong hold on these electrons i. e. should be a weak reducing agent.

- One never comes across an absolutely pure oxidising or reducing agent. Their solutions always contain the products of their reduction or oxidation respectively.
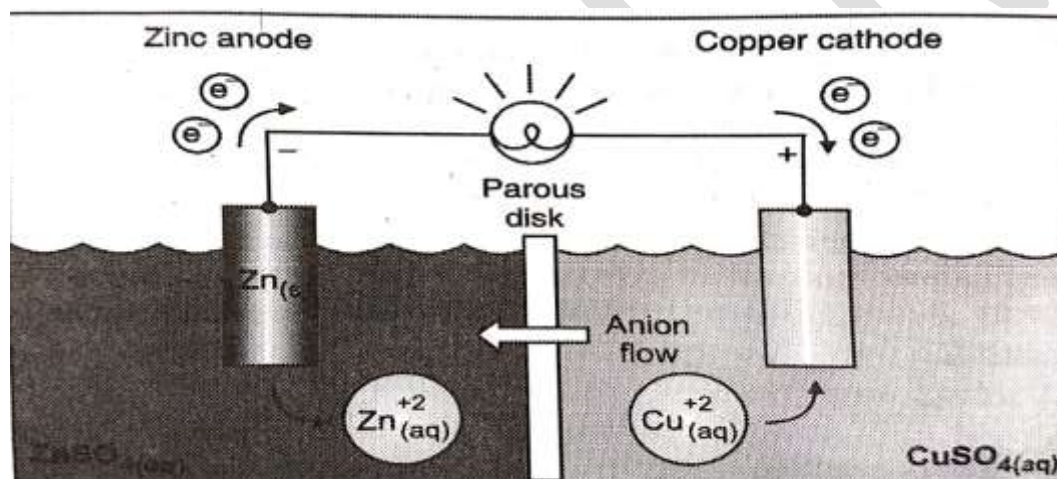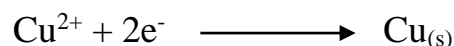

Reaction:

At Zn anode, oxidation takes place (the metal loses electrons). This is represented in the following oxidation half-reaction.

$$Zn_{(s)} \longrightarrow Zn^{2+} + 2e^-$$
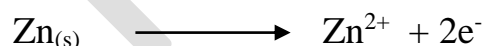
At the Cu cathode, reaction takes place (electrons are accepted). This is represented in the following reduction half-reaction.

$$Cu^{2+} + 2e^- \longrightarrow Cu_{(s)}$$

Combined reaction: $Zn_{(s)} + CuSO_{4(aq)} \longrightarrow ZnSO_{4(aq)} + Cu_{(s)}$

Equivalent weight of oxidizing and reducing agent

In a redox reaction, one of the reacting entities is oxidizing agent and the other entity is reducing agent. There are two methods to calculate equivalent weight in redox reaction.

1. The number of electrons involved in the reaction. (Ion-Electron Balance Method)

2. The change in the oxidation number of significant element in the oxidant or reductant. (Oxidation Number Method)

1. Ion-Electron Balance Method

The oxidizer is recipient of electrons, whereas reducer is releaser of electrons. The number of electrons transferred from one entity to another to balance the redox reaction. So equivalent weight is calculated.

$$\text{Equivalent weight of OA} = \frac{Mol.\,Weight}{Number\ of\ electrons\ gained\ by\ one\ molecule}$$

❖ For example-

Ex.1 Potassium permanganate in acidic condition a strong oxidizer It means it gains five electrons during redox rection.

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$
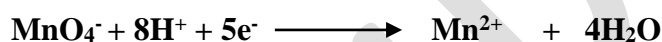
Equivalent weight of $KMnO_4 = \frac{158}{5} = 31.6$ gm

Ex.2 Potassium permanganate in neutral condition gives following rection.

$$MnO_4^- + 4H^+ + 3e^- \longrightarrow MnO_2 + 2H_2O$$

Equivalent weight of $KMnO_4 = \frac{158}{3} = 52.66$ gm

Ex.3 Potassium dichromate in acidic condition a strong oxidizer. It means it gains six electrons during redox rection. Potassium dichromate in acidic solution results in:
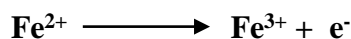
$$K_2Cr_2O_7 + 14H^+ + 6e^- \longrightarrow 2K^+ + 2Cr_3^+ + 7H_2O$$

Equivalent weight of $K_2Cr_2O_7 = \frac{294.26}{6} = 49$ gm

$$\text{Equivalent weight of RA} = \frac{Mol.\,Weight}{Number\ of\ electrons\ lost\ by\ one\ molecule}$$

❖ For example:

Ex.1 Redox reaction of ferrous sulphate; ferrous (Fe^{2+}) ions lose its electron during redox rection.

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

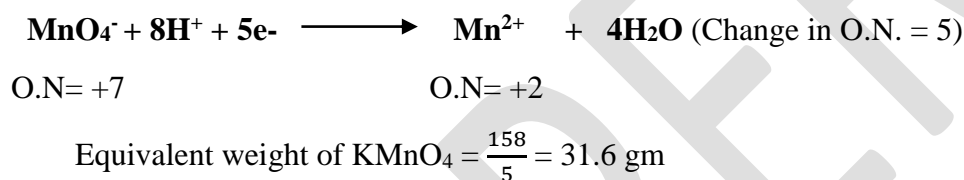Equivalent weight of Ferrous Sulphate = 278/1 = 278 gm $FeSO_4$

2. Oxidation Number Method

In Redox Titration, Equivalent weight is also calculated by taking the change in valency or oxidation no. of oxidizing or reducing agent during redox titration.

Valency of an element represents the no. of electron, which its atom takes on or gives on to reacting element to form compound.

$$\text{Equivalent weight of OA/RA} = \frac{Mol.\,Weight}{Change\ in\ oxidation\ Number\ per\ mole}$$

❖ **Ex.1** Potassium permanganate in acidic condition a strong oxidixzer. It is reduced and its oxidation number is reduced from +7 to +2. Therefore change in oxidation number is 5.

$$MnO_4^- + 8H^+ + 5e- \longrightarrow Mn^{2+} + 4H_2O \text{ (Change in O.N. = 5)}$$

O.N= +7   O.N= +2

Equivalent weight of $KMnO_4 = \frac{158}{5} = 31.6$ gm

Ex.2 Redox reaction of ferrous sulphate; ferrous (Fe^{2+}) ions converted into ferric ion in which oxidation number increases by 1.

$$Fe^{2+} \longrightarrow Fe^{3+} + e^- \text{ (Change in O.N. = 1)}$$

O.N= +2   O.N= +3
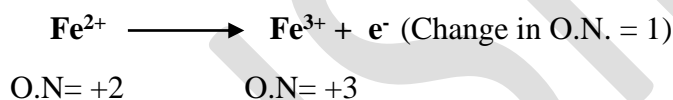
❖ Equivalent weight of Ferrous Sulphate = 278/1 = 278 gm $FeSO_4$

Thus it indicates that, the valence factor for either an oxidizing or reducing agent is equal to the numbers of electron transferred from one entity to another.

DETECTION OF END POINT

1) By using Redox indicator

There are three types of indicators used in redox titration.

  I.   Redox indicators/ Internal Indicators

 II.   Self-indicators

III.   External indicator

2) Potentiometric method
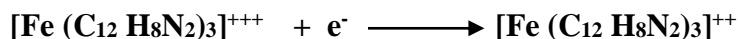
❖ **By using Redox indicator**

1. Internal Indicator

An oxidation-reduction indicator is a compound which exhibits different colours in the oxidised and reduced forms.

$$In_{oxi} + ne^- = In_{(red)}$$

One of the best redox indicator is the Ferroin, (ortho phenanthroline ferrous ion).

The base combines readily in solution with ferrous salts in the molecular ratio 3 base: 1 ferrous ion forming the intensely red tri ortho phenanthroline ferrous ion.

With strong oxidizing agent the ferric complex ion is formed which has a pale blue colour.

$$[Fe\ (C_{12}\ H_8N_2)_3]^{+++}\ \ +\ e^-\ \longrightarrow\ [Fe\ (C_{12}\ H_8N_2)_3]^{++}$$

(Oxidised form = pale blue)   (Reduced form = Red)

- **Examples of Redox Indicators**

INDICATOR NAME	COLOUR CHANGE	
	Oxidized	**Reduced**
Nitroferroin	Pale blue	Red
Ferroin	Pale blue	Red
N-phenyl anthranilic acid	Purple- Red	Colourless
Diphenylamine in conc. Sulphuric acid	Red-violet	Colourless
Diphenylamine	Violet	Colourless
Starch indicator	Blue	Colourless

2. Self-Indicator

Many times he titrant itself may be so strongly coloured after the end point, in that case titrant acts as self-indicator. One drop of $KMnO_4$ imparts visible colour change to hundred/thousand ml of solution.

E.g. $KMnO_4$ – Pink, Iodine- Brown, $Ce(So_4)_2$- Pale yellow

$KMnO_4$ is strongly used as self-indicators. $KMnO_4$ get reduced in the redox titration as:

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+}\ +\ 4H_2O$$
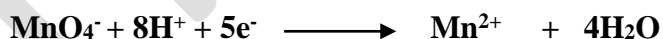
The $KMnO_4$ has dark purple colour due to MnO_4^- which on reduction give Mn^{2+} which is colourless, so as at the end point excess drop of $KMnO_4$. It get dilute in the solution and gives pink colour to the solution.

3. External Indicator

The best known example of an external indicator in redox process is the spot test for the titration of ferrous ion with $K_2Cr_2O_7$.

Near the equivalence point, drops of solution are removed and brought into contact with dilute freshly prepared potassium ferricyanide solution on a spot plate.

The end point is reached when first drop fails to give blue color. These are almost obsolete now-a-days as there are various better internal indicator available, further there is loss of reaction mixture.

❖ **Potentiometric Methods**

This is physico-chemical method which may be applied to those cases where suitable indicators, are not available.

This method is also applied to those cases in which the visual indicator method fails or is of limited accuracy e.g. for coloured solution for very dilute solution.

TYPES OF REDOX TITRATION

1. Permanganate Titration
2. Iodine Titration
3. Dichromate titration
4. Ceriometry
5. Potassium bromate titration
6. Titration with potassium iodate

1) Permanganate Titration
Principle:

Titrations involving permanganate oxidation is a special case of oxidimetry in which a solution of $KMnO_4$ is used as an oxidant.

The ability of $KMnO_4$ solution to oxidise is due to the conversion of the MnO_4^- to Mn^{2+} in acidic solution and to MnO_2 in alkaline, neutral or very weak acidic solution. The MnO_4^- is reduced in accordance with the following reactions:

In Acidic solution

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$
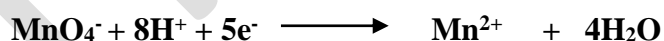
In Alkaline or Neutral solution

$$MnO_4^- + 4H^+ + 3e^- \longrightarrow MnO_2 + 2H_2O$$
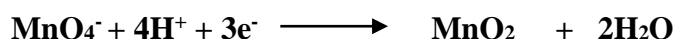
In acidic solution,

Solutions containing MnO_4^- ions (in oxidized state) are purple in colour, solution of salts containing Mn^{2+} (reduced $KMnO_4$) ions are colourless hence a permanganate solution is decolourised when added to the solution of reducing agent as long as latter is present in the solution.

The moment there is an excess of $KMnO_4$ the solution it becomes pink or purple. Thus permanganate ion can serve as its own indicator, especially in acidic solution.

In Alkaline and Neutral solution,

In alkaline and neutral solution, MnO_4^- reduces in to MnO_2. These MnO_2 is in the form of brown particles, therefore $KMnO_4$ is not used as self-indicator.

Here, diphenylamine (red-violet to colourless) or phenylanthranillic acid (purple-red) is used as an indicator with very dilute solution of $KMnO_4$.

$KMnO_4$ solution is used in determination of both oxidizing and reducing agents.

❑ **Preparation of $KMnO_4$, solution 0.02 M:**

Dissolve 3.2 g of potassium permanganate in water to make 1000 ml, heat on water bath for 1 hour, allow to stand for 2 days, filter through glass wool.
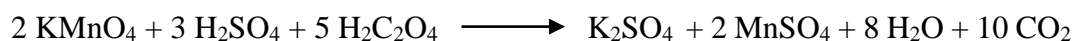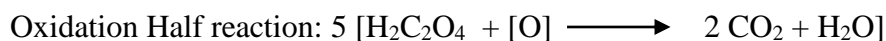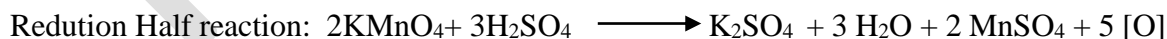
❑ **Standardization of 0.02 M $KMnO_4$**

(A) With $Na_2S_2O_3$: It can be standardized by using sodium thiosulfate. To 25 ml of above solution in the stoppered flask add 2 g of potassium iodide, followed by 10 ml of sulfuric acid. Titrate the liberated iodine with 0.1 M sodium thiosulfate solution using 3 ml of starch solution as indicator. Perform the blank determination and make necessary correction.

(B) With Oxalic Acid ($H_2C_2O_4$):

$KMnO_4$ solution is standardized against chemically pure oxalic acid.

Make 0.1 N solution of oxalic acid. Add 20 ml of this solution in conical flask. Add 5 ml of conc. H_2SO_4. Warm it up to 70 °C and titrate against 0.1 N $KMnO_4$. At the end point pink colour is observed.

Reduction of MnO_4^-: $2[MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O]$

Oxidation of $C_2O_4^{2-}$: $5 [C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-]$

Redution Half reaction: $2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 3 H_2O + 2 MnSO_4 + 5 [O]$

Oxidation Half reaction: $5 [H_2C_2O_4 + [O] \longrightarrow 2 CO_2 + H_2O]$

$2 KMnO_4 + 3 H_2SO_4 + 5 H_2C_2O_4 \longrightarrow K_2SO_4 + 2 MnSO_4 + 8 H_2O + 10 CO_2$

In these reaction, MnO_4^- is reduced to Mn^{+2} and $C_2O_4^{2-}$ is oxidized to CO_2. The oxidation number of carbon in $C_2O_4^{2-}$ changes from +3 to +4.

(B) With Arsenic Trioxide (AS_2O_3): weigh accurately 0.25 gm arsenic trioxide (AS_2O_3). Add 10 ml of water and allow to stand it.

Thus, AS_2O_3 dissolve in water to convert into Arsenious trioxide.

Further add 100 ml water and 10 ml pure conc. H_2SO_4. Add 1 drop of 0.0025 M potassium iodide or potassium iodate (KIO_3) as a catalyst. Add $KMnO_4$ solution from burette. Faint pink colour is observed for 30 second at the end point.

Reaction: $AS_2O_3 + 3 H_2O \longrightarrow 2 H_3AsO_3$ (conversion into Arseniuos acid)

Reduction of $KMnO_4$: $2 [MnO_4^- + 8 H^+ + 5e^- \longrightarrow Mn^{+2}]$

Oxidation of Arsenious acid: $5 [H_3AsO_3 + H_2O \longrightarrow H_3AsO_4 + 2 H^+ + 2e^-]$

$KMnO_4$ titrations used in analysis of $FeSO_4$, H_2O_2 and etc.

2) Iodine Titrations

Titration involving iodine are two types: **(1) Iodimetric**
                                        (2) Iodometric.

Iodimetry covers the titrations with the standard solution of Iodine, while Iodometry deals with the titration of iodine liberated in chemical reaction.

❖ **Iodimetry (Iodimetric titration)**

It is a titration in which iodine solution directly titrate with reducing agent using starch as an indicator or iodine act as a self-indicator.

This titration is carried out in neutral or slightly alkaline condition.

❑ **Preparation of Iodine solution (0.05 M):**

Take 14 g of iodine and 36 gm of KI (potassium iodide), dissolve it in 100 ml water 3 drops of HCl are added and dilute it to 1000 ml.
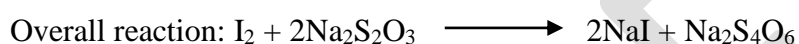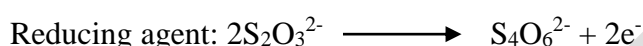
❑ **Standardization of Iodine solution:**
Standardization of I_2 solution is done with sodium thiosulphate and arsenic trioxide.

(A) Standardization I_2 solution with Sodium thiosulphate ($Na_2S_2O_3$):

- Preparation of 0.1 M $Na_2S_2O_3$: Add 25 gm of $Na_2S_2O_3$ and 0.2 gm of Na_2CO_3 in water and make up the volume upto 1000 ml with CO_2 free water.

- Standardization:
  Directly titrate prepared iodine solution against sodium thiosulphate ($Na_2S_2O_3$) until the solution has a pale yellow colour. Add starch solution and continue the titration until the solution is colourless.

Here, solution changes from **blue colour to colourless** because before end point there is a presence of I_2 in reaction mixture and thus starch indicator gives blue colour with it. When I_2 is over in solution (at the time of end point) then solution becomes colourless because all I_2 are consumed and only I^- ions are present with starch indicator which do not give any colour.

Sometimes, Iodine serves as self-indicator because solution of Iodine has intense yellow to brown colour. Addition of 1 drop of 0.1 N I_2 solution gives pale yellow colour to 100 ml water. Thus, Iodine solution serves as its own indicator.

Reaction:

Oxidizing agent: $I_2 + 2e^- \longrightarrow 2I^-$

Reducing agent: $2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e^-$

Overall reaction: $I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$

Here, $I_2 = 2Na_2S_2O_3 = 2e^-$
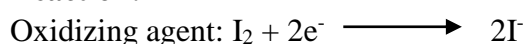
(B) Standardization I_2 solution with Arsenic Trioxide (AS_2O_3):

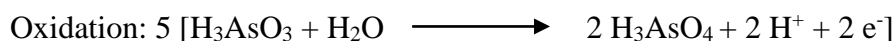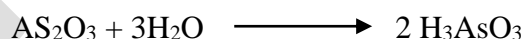This is a best primary standard for Iodine solution.

Weigh accurately 0.15 g of arsenic trioxide previously dried at 105 °C for 1 hour. Dissolve it in 20 ml of 1 M NaOH by warming and dilute with 40 ml of water. Add 0.1 ml of methyl orange solution.

Add dropwise dilute HCl until yellow colour changed to pink. Add 2 gm of Na_2CO_3 and dilute with 50 ml of water. Add 3 ml of starch solution. Titrate with iodine until a permanent blue colour is produced.

Each ml of 0.05 M iodine is equivalent to 0.004946 g of As_2O_3.

Reaction:

As_2O_3 is dissolved in water to give Arsenious acid (H_3AsO_3).

$$AS_2O_3 + 3H_2O \longrightarrow 2 H_3AsO_3$$

Reduction: $As_2O_3 + 3 H_2O \longrightarrow 2 H_3AsO_3$

Oxidation: $5 [H_3AsO_3 + H_2O \longrightarrow 2 H_3AsO_4 + 2 H^+ + 2 e^-]$

Overall reaction: $H_3AsO_3 + I_2 + H_2O \longrightarrow HASO_4^{2-} + 4 H^+ + 2I^-$

Here, colour change occurs from **colourless to blue colour** at the end point due to conversion of Iodine (I_2) to Iodide ion (I^-) will not occur after all Arsenious acid are

consumed. So, at the end point extra drop of Iodine will remain as such as in reaction mixture and thus solution becomes blue in colour.
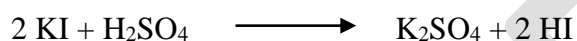
❖ Iodometry (Iodometric titration):

In Iodometry, formation of iodine takes place when $KBrO_3$ / KIO_3 / $K_2Cr_2O_7$ reacts with KI (Potassium iodide) in acidic condition.

Reaction:

If HCl used,

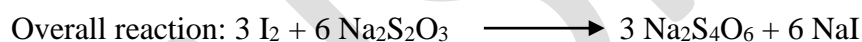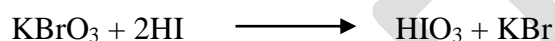$$KI + HCl \longrightarrow HI + KCl$$

If H_2SO_4 used,

$$2 KI + H_2SO_4 \longrightarrow K_2SO_4 + 2 HI$$

Here, HI (Hydroiodic acid) reacts with oxidizing agent.

$$KBrO_3 + 2HI \longrightarrow HIO_3 + KBr$$

$$IO_3^- + 5 I^- + 6H^+ \longrightarrow 3 I_2 + 3 H_2O \text{ [Liberation of } I_2]$$

Reduction: $3 [I_2 + 2 e^- \longrightarrow 2 I^-]$ Free iodine converted into I^-

Oxidation: $2 S_2O_3^- \longrightarrow S_4O_6^{2-} + 2 e^-$

Overall reaction: $3 I_2 + 6 Na_2S_2O_3 \longrightarrow 3 Na_2S_4O_6 + 6 NaI$

Here, starch indicator is used to detect end point because starch forms complex with liberated iodine (I_2) and colour of that complex is blue. When all I_2 are consumed in reaction with sodium thiosulphate, only iodide ions (I^-) are present in solution and thus solution becomes colourless.

Conditions for Iodometric determination:

1) As the potential of the $I_2/2I^-$ is not high, many iodometric reactions are reversible and do not go to completion. Only if suitable condition provided, the reaction will undergo completion.

2) Since, Iodine is volatile, titration is conducted in the cold condition. Also sensitivity of starch diminishes with rise in temperature.

3) Iodometric titration cannot be performed in strongly alkaline solution as it forms hypoiodide.

$$2 NaOH + I_2 \longrightarrow NaOI + NaI + H_2O$$
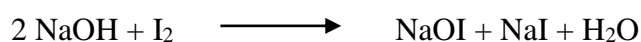
If the reaction results in formation of H^+ ion, they must be removed to ensure that reaction proceeds partially to completion in required direction.

$$HCO_3^- + H^+ \longrightarrow H_2CO_3 \longrightarrow H_2O + CO_2$$

4) The rate of reaction between iodate (IO_3^-) and iodide (I^-) ion is too slow. Therefore sufficient time should be given for completion of reaction.

5) Iodine is very slightly soluble in water, so there is need to add excess of KI to dissolve the I_2.

$$I_2 + KI \longrightarrow KI_3$$
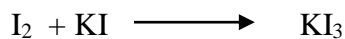
6) The reaction mixture is kept in dark place, because light accelerates the side reaction in which I^- ions are oxidized to I_2 by atmospheric oxygen.

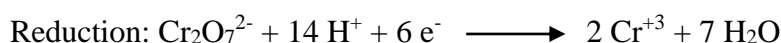$$4\,I^- + 4\,H^+ + O_2 \longrightarrow 2\,I_2 + 2\,H_2O$$
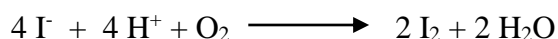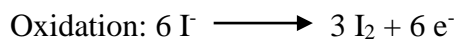
Example: Standardization of $Na_2S_2O_3$ with $KBrO_3$.

IODIMETRIC TITRATION	IODOMETRIC TITRATION
It is direct titration of iodine	It is an indirect titration of I_2. (I_2 liberates in the reaction between KIO_3 + KI)
Iodine is used as a titrant.	Iodine is not used as a titrant but KIO_3 are used as titrant which reacts with KI.
It is carried out in neutral or slightly alkaline solution, because it form hypoiodate ion from I_2 which is strong oxidizing agent.	It is carried out in slightly acidic condition. In strongly alkaline solution hypoiodide ion is formed. $2NaOH + I_2 \longrightarrow NaOI + NaI + H_2O$
It is used for analysis of reducing agent. I_2 is oxidizing agent (Titrant) Arsenic oxide & $Na_2S_2O_3$ are reducing agent. (Analyte)	It is used for analysis of oxidizing agent. $Na_2S_2O_3$ is reducing agent. (Titrant) $K_2Cr_2O_7$ & KIO_3 are oxidizing agent (Analyte)

(A) Standardization of Sodium thiosulphate ($Na_2S_2O_3$) with potassium dichromate ($K_2Cr_2O_7$):

$K_2Cr_2O_7$ is a primary standard which is to be dissolved in water and acidified with HCl. Excess of KI is added.

Here $K_2Cr_2O_7$ oxidizes KI to Iodine. Liberated iodine is titrated with thiosulfate using starch indicator till pale green colour is achieved.

$$K_2Cr_2O_7 + 6\,KI + 7\,H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + 3\,I_2 + 4\,K_2SO_4 + 7\,H_2O$$

Reduction: $Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- \longrightarrow 2\,Cr^{+3} + 7\,H_2O$

Oxidation: $6 I^- \longrightarrow 3 I_2 + 6 e^-$

(B) Standardization of Sodium thiosulphate ($Na_2S_2O_3$) with potassium Iodate ($K_2Cr_2O_7$):

KIO_3 is a primary standard which reacts with KI in acid solution and liberates I_2 which give pale yellow colour to solution.

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

3) Dichromate Titrations

Potassium dichromate is not such a powerful oxidizing agent as $KMnO_4$.
But there are some advantages of $K_2Cr_2O_7$ over $KMnO_4$. $K_2Cr_2O_7$ is always obtain in pure form. It is stable upto its fusion point.
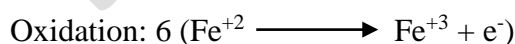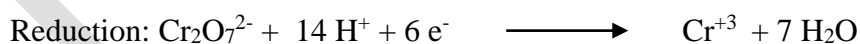
▪ **Preparation of $K_2Cr_2O_7$:**
Standard solution of exactly known concentration can be prepared by weighing out the pure drug salt and dissolving it in a proper volume of water.

- Potassium dichromate is used only in acid solution (acid concentration does not exceed 1 to 2 M). In acidic solution potassium dichromate is reduced to a green chromium (III) salt. It is not reduced by cold HCl.

$$Cr_2O_7^{2-} \longrightarrow 2 Cr^{3+} \text{ (Green)}$$

- Compared with $KMnO_4$ solution, dichromate is less easily reduced by organic matter.

- $K_2Cr_2O_7$ is used in determination of iron in iron ores. Ore is dissolved in HCl. Iron (III) is reduced to Iron (II).

- Solution of iron (III) is titrated with standard dichromate solution. In acid solution, $K_2Cr_2O_7$ is reduced.

$$Cr_2O_7^{2-} + 6 Fe^{2+} + 14 H^+ \longrightarrow 2 Cr^{3+} + 6 Fe^{3+} + 7 H_2O$$

Reduction: $Cr_2O_7^{2-} + 14 H^+ + 6 e^- \longrightarrow Cr^{+3} + 7 H_2O$

Oxidation: $6 (Fe^{+2} \longrightarrow Fe^{+3} + e^-)$

- The green colour due to the Cr^{+3} ions are formed by the reduction of $K_2Cr_2O_7$ makes it impossible to detect end point by simple visual inspection. Redox indicator must be applied which give strong colour change.

- Mostly external indicator is widely used. For e.g. N-phenylanthranillic acid (0.1% solution in 0.005 M) and sodium diphenylamine sulphonate (0.2 % solution).

PROCEDURE:

❖ **Preparation of $K_2Cr_2O_7$ (0.02 M):**

Powder 6 gm of $K_2Cr_2O_7$ and heat at 140-150 °C (50 -60 min) and allow to cool in a closed vessel in desiccator.

Weigh out accurately about 5.88 g of the dry potassium dichromate into a weighing bottle. Transfer in 1 L graduated flask using a small funnel to avoid loss.

Dissolve the salt in the flask in water and make upto mark. Shake well.

❖ **PROCEDURE FOR OXIDATION WITH POTASSIUM DICHROMATE**

Iron ore into solution with conc. HCl results in reduction of iron (III) to iron (II) by use of tin (II) chloride. Solution turns into green colour.

Now, Iron (II) solution is diluted with 100 ml water and 100 ml of 1.5 M H_2SO_4. 5 ml of 85 % phosphoric acid is also added.

Finally add 6-8 drops of sodium diphenylamine sulphonate indicator and titrate slowly with standard dichromate until the colour changes from green colour to violet colour.

4) Ceriometry Titrations (Oxidation with cerium (IV) sulphate solution):

Cerium sulphate is powerful oxidizing agent with reduction potential in 0.5 to 4.0 M sulphuric acid at 25 °C is 1.43 ± 0.05 V.

It can be used only in acid solution best in 0.5 M or higher concentration. In neutral solution ceric hydroxide (or hydrated cerium (IV) oxide) or basic salts are precipitated.

The solution of cerium (IV) sulphate has intense yellow colour and in hot solutions which are not too dilute, the end point may be detected without an indicator. This procedure requires blank correction, and it is therefore preferable to add a suitable indicator.

- As standard oxidizing agent, Cerium (IV) sulphate has four advantages.

    1. Cerium (IV) sulphate solutions are stable over prolonged periods. They need not be protected from light, and may even be boiled for a short time without appreciable change in concentration. The stability of sulphuric acid solutions covers the wide range of 10-40 mL of concentrated sulphuric acid per litre. It is evident, therefore, that an acid solution of cerium (IV) sulphate surpasses a permanganate solution in stability.

2. Cerium (IV) sulphate may be employed in the determination of reducing agents in the presence of a high concentration of hydrochloric acid.

3. Cerium (IV) solutions in 0.1 M solution are not too highly coloured to obstruct vision when reading the meniscus in burettes and other titrimetric apparatus.

4. In the reaction of cerium (1V) salts in acid solution with reducing agents, the simple change is assumed to take place. With permanganate, of course, a number of reduction products are produced according to the experimental conditions.

$$Ce^{4+} + e \longrightarrow Ce^{3+}$$

Solutions of cerium (1V) sulphate in dilute sulphuric acid are stable even at boiling temperatures. Hydrochloric acid solutions of the Salt are unstable because of reduction to cerium (II1) by the acid with the simultaneous liberation of chlorine:

$$2\ Ce^{4+} + 2\ Cl^- \longrightarrow 2\ Ce^{3+} + Cl_2$$
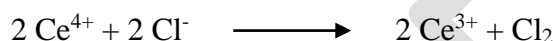
This reaction takes place quite rapidly on boiling, and hence hydrochloric acid cannot be used in oxidations which require boiling with excess of cerium (IV) sulphate in acid solution: sulphuric acid must be used in such oxidations.

However, direct titration with cerium (IV) sulphate in a dilute hydrochloric acid medium, e.g. for iron (II) may be accurately performed at room temperature, and in this respect cerium (IV) sulphate is superior to potassium permanganate.

The presence of hydrofluoric acid is harmful, since fluoride ion forms a stable çomplex with Ce (IV) and decolorises the yellow solution.

**Preparation of 0.1 M Cerium (IV) sulphate:**

Weigh 35-36 g pure cerium (IV) sulphate in 500 ml beaker. Add 56 ml of 1:1 mixture of H_2SO_4 and water and stir, with frequent additions of water and gentle warming, until the Salt is dissolved.

▪ **STANDARDISATION OF CERIUM (IV) SULPHATE SOLUTIONS**

(A) Standardization of Cerium (IV) sulphate with arsenic (II1) oxide:
The arsenic (II1) oxide is dissolved in sodium hydroxide solution, the solution acidified with dilute sulphuric acid, and after adding 2 drops of an 'osmic acid' solution prepared by dissolving 0.1 g osmium tetroxide in 40 mL of 0.05 M sulphuric acid, and the indicator (1-2 drops ferroin or 0.5 mL N-phenylanthranilic acid) is added.

It is titrated with the cerium (IV) sulphate solution to the first sharp colour change: orange-red to very pale blue or yellowish-green to purple respectively.

$$2\ Ce^{3+} + H_3AsO_3 + H_2O \longrightarrow 2\ Ce^{3+} + H_3AsO_4 + 2H^+$$
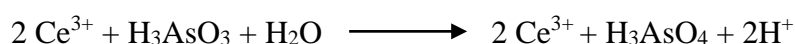
Procedure: Weigh out accurately about 0.2 g of arsenic (III) oxide, previously dried at 105-110 °C for 1-2 hours, and transfer to a 500 ml beaker. Add 20 ml of approximately 2 M sodium hydroxide solution, and warm the mixture gently until the arsenic (III) oxide has completely dissolved.

Cool to room temperature, and add 100 ml water, followed by 25 ml 2.5 M sulphuric acid. Then add 3 drops 0.01 M osmium tetroxide solution.

Titrate with the 0.1 M cerium (IV) sulphate solution until the first sharp colour change occurs. Repeat with two other samples of approximately equal weight of arsenic (III) oxide.

(B) Standardization with sodium oxalate:
Standardisation may also be carried out with sodium oxalate; in this case, an indirect procedure must be used as the redox indicators are themselves oxidised at the elevated temperatures which are necessary.

The procedure, therefore, is to add an excess of the cerium (IV) solution, and then, after cooling, the excess is determined by back-titration with an iron (II) solution. It is possible to carry out a direct titration of the sodium oxalate if a potentiometric procedure is used.

Procedure:
Prepare an approximately 0.1 M solution of ammonium iron (II) sulphate in dilute sulphuric acid and titrate with the cerium (IV) sulphate solution using ferroin indicator.

Weigh out accurately about 0.2 g sodium oxalate into a 250 mL conical flask and add 25-30 mL 1 M sulphuric acid. Heat the solution to about 60 °C and then add about 30 mL of the cerium (IV) solution to be standardised dropwise, adding the solution as rapidly as possible consistent with drop formation.

Re-heat the solution to 60 °C, and then add a further 10 mL of the cerium (IV) solution. Allow to stand for three minutes, then cool and back-titrate the excess cerium (IV) with the iron (II) solution using ferroin as indicator.

5) Potassium Bromate Titrations
Potassium bromate is a powerful oxidising agent which is reduced smoothly to bromide:

$$BrO_3^- + 6\ H^+ + 6e \rightleftharpoons Br^- + 3\ H_2O$$
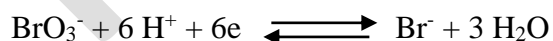
The relative molecular mass is 167.00, and a 0.02M solution contains 3.34 g/L -'potassium bromate. At the end of the titration free bromine appears:

$$BrO_3^- + 5Br + 6\ H^+ \rightleftharpoons 3\ Br_2 + 3\ H_2O$$
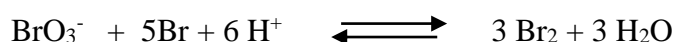
Due to the presence of free bromine, and consequently the end-point, can be detected by its yellow colour, but it is better to use indicators such as methyl orange, methyl red, naphthalene black 12B, xylidine ponceau, and fuchsine.

These indicators have their usual colour in acid solution, but are destroyed by the first excess of bromine.

Direct titrations with bromate solution in the presence of irreversible dyestuff indicators are usually made in hydrochloric acid solution, the concentration of which should be at least 1.5-2M. At the end of the titration some chlorine may appear by virtue of the reaction:
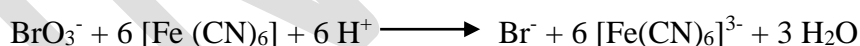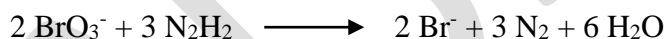
$$10\ Cl^- + 2BrO_3 + 12H^+ = 5Cl_2 + Br_2 + 6H_2O$$

The titrations should be carried out slowly so that the indicator change, which is a time reaction, may be readily detected. Otherwise colour change cannot be easily detected.

With the highly coloured indicators (xylidine ponceau, fuchsine, or naphthalene black 12B), the colour fades as the end point is approached and another drop of indicator can be added. At the end point the indicator is irreversibly destroyed and the solution becomes colourless or almost so.

If the fading of the indicator is confused with the equivalence point, another drop of the indicator may be added. If the indicator has faded, the additional drop will colour the solution; if the end point has been reached, the additional drop of indicator will be destroyed by the slight excess of bromate present in the solution.

Examples of determinations utilising direct titration with bromate solutions are expressed in the following equations:

$$BrO_3^- + 3\ H_3AsO_3 \longrightarrow Br^- + 3\ H_3AsO_4$$

$$2\ BrO_3^- + 3\ N_2H_2 \longrightarrow 2\ Br^- + 3\ N_2 + 6\ H_2O$$

$$BrO_3^- + NH_2OH \longrightarrow Br^- + NO_3^- + H^+ + H_2O$$

$$BrO_3^- + 6\ [Fe\ (CN)_6] + 6\ H^+ \longrightarrow Br^- + 6\ [Fe(CN)_6]^{3-} + 3\ H_2O$$

Various substances cannot be oxidised directly with potassium bromate, but react quantitatively with an excess of bromine. Acid solutions of bromine of exactly known concentration are readily obtainable from a standard potassium bromate solution by adding acid and an excess of bromide.

$$BrO_3^- + 5\ Br^- + 6\ H^+ = 3\ Br_2 + 3\ H_2O$$

In this reaction 1 mole of bromate yields six atoms of bromine. Bromine is very volatile, and hence such operations should be conducted at as low a temperature as possible and in conical flasks fitted with ground-glass stoppers.

The excess of bromine may be determined iodometrically by the addition of excess of potassium iodide and titration of the liberated iodine with standard thiosulphate solution:

$$2\ I^- + Br_2 = I_2 + 2\ Br^-$$
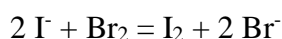
6) Titration with potassium iodate

Potassium iodate is a powerful oxidising agent. Iodate is reduced to iodine in the presence of reducing agent.

This reaction of conversion into iodine stops when the reaction between potassium iodate and reducing agents such as iodide ion or arsenic (III) oxide in solutions of moderate acidity (0.1 - 2.0 M hydrochloric acid) occurs.

$$IO_3^- + 5\ I^- + 6\ H^+ = 3\ I_2 + 3\ H_2O$$

$$2\ IO_3^- + 5\ H_3AsO_3 + 2\ H^+ = I_2 + 5\ H_3AsO_4 + H_2O$$

As already indicated, the first of these reactions is very useful for the generation of known amounts of iodine, and it also serves as the basis of a method for standardising solutions of acids.

With a more powerful reductant, e.g. titanium (III) chloride, the iodate is reduced to iodide:

$$IO_3^- + 6\ Ti^{3+} + 6H^+ = I^- + 6\ Ti^{4+}\ 3\ H_2O$$
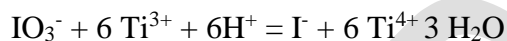
In more strongly acid solutions (3-6M hydrochloric acid) reduction occurs to iodine monochloride, and it is under these conditions that it is most widely used.

$$IO_3^- + 6\ H^+ + Cl^- + 4e \rightleftharpoons ICl + 3H_2O$$

In hydrochloric acid solution, iodine monochloride forms a stable complex ion with chloride ion:

$$ICl + Cl^- \rightleftharpoons ICl_2^-$$

The overall half-cel1 reaction may therefore be written as:

$$IO_3^- + 6H^+ + 2Cl^- + 4e \rightleftharpoons ICl_2^- + 3\ H_2O$$
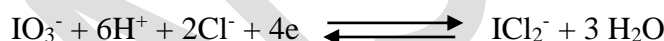
The reduction potential is 1.23 volts; hence under these conditions potassium iodate acts as a very powerful oxidising agent.

Oxidation by iodate ion in a strong hydrochloric acid medium proceeds through several stages:

$$IO_3^- + 6\ H^+ + 6e \rightleftharpoons I^- + 3\ H_2O$$

$$IO_3^- + 5\ I^- + 6\ H^+ \rightleftharpoons 3\ I_2 + 3\ H_2O$$

$$IO_3^- + 2I_2 + 6\ H^+ \rightleftharpoons 5\ I^+ + 3\ H_2O$$
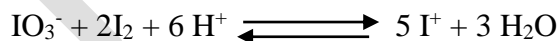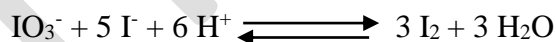
In the initial stages of the reaction free iodine is liberated: as more titrant is added, oxidation proceeds to iodine monochloride, and the dark colour of the solution gradually disappears. The overall reaction may be written as:

$$IO_3^- + 6\ H^+ + 4e \rightleftharpoons I^+ + 3\ H_2O$$
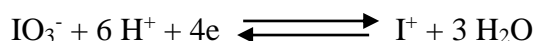
The reaction has been used for the determination of many reducing agents.

Under these conditions starch cannot be used as indicator because the characteristic blue colour of the starch-iodine complex is not formed at high concentrations of acid.

The end point is marked by the disappearance of the last trace of violet colour, due to iodine, from the solvent: iodine monochloride is not extracted and imparts a pale yellowish colour to the aqueous phase.

Certain dyes are used as indicator e.g. amaranth: colour changes red to colourless. The indicators are used as 0.2 per cent aqueous solutions and about 0.5 mL per titration is added near the end point.

The dyes are destroyed by the first excess of iodate, and hence the indicator action is irreversible.

p-Ethoxychrysoidine is a moderately satisfactory reversible indicator. It is used as a 0.1 per cent solution in ethanol (about 12 drops per titration), and the colour change is from red to orange; the colour is red-purple just before the end point.

PREPARATION OF 0.025M POTASSIUM IODATE

Dry some potassium iodate at 120 OC for 1 hour and allow it to cool in a covered vessel in a desiccator.

Weigh out exactly 5.350 g of the finely powdered potassium iodate on a watchglass, and transfer it by means of a clean camel-hair brush directly into a dry 1 L graduated flask.

Add about 400-500 mL of water, and gently rotate the flask until the Salt is completely dissolved. Make up to the mark with distilled water. Shake well.

$$IO_3^- + 6 H^+ + Cl^- + 4e \; \rightleftharpoons \; ICl + 3H_2O$$

Example: To assay a sample of arsenic (II1) oxide the following procedure may be used.

Procedure:

Weigh out accurately about 1.1 g of the oxide sample, dissolve in a small quantity of warm 10 per cent sodium hydroxide solution, and make up to 250 mL in a graduated flask. Add 25 mL water, 60 mL concentrated hydrochloric acid and about 5 mL carbon tetrachloride or chloroform.

Cool to room temperature. Run in the standard 0.025M potassium iodate from a burette until the solution, which at first is strongly coloured with iodine, becomes pale brown.

Continue to add small volumes of the iodate solution, shaking vigorously after each addition, until the organic layer is only very faintly violet.

Continue the addition dropwise, with shaking after each drop, until the solvent loses the last trace of violet and has only a very pale yellow colour (due to iodine chloride). The end point is very sharp.