# Analytical chemistry

Lecture №22

## REDOX titration
## Part I

# Titration Methods Involving the Use of Iodine or the Formation of Iodine

Iodine is an oxidizing agent that can be used to titrate fairly strong reducing agents. On the other hand, iodide ion is a mild reducing agent and serves as the basis for determining strong oxidizing agents.

Iodine is a moderately strong oxidizing agent and can be used to titrate reducing agents. Titrations with **$I_2$** are called ***iodimetric methods.***

$$I_3^- + 2e^- \rightleftharpoons 3I^- \qquad E^0 = 0.536\ \text{V}$$

These titrations are usually performed in neutral or mildly alkaline (pH 8) to weakly acidic solutions. If the pH is too alkaline, $I_2$ will disproportionate to hypoiodate and iodide:

$$I_2 + 2OH^- \rightleftharpoons IO^- + I^- + H_2O$$

There are three reasons for keeping the solution from becoming strongly acidic. First, the starch used for the end-point detection tends to hydrolyze or decompose in strong acid, and so the end point may be affected. Second, the reducing power of several reducing agents is increased in neutral solution. The third reason for avoiding acid solutions is that the $I^-$ produced in the reaction tends to be oxidized by dissolved oxygen in acidic solution

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

# Properties of Iodine Solutions

Iodine is not very soluble in water. To prepare solutions having analytically useful concentrations of the element, iodine is usually dissolved in moderately concentrated solutions of potassium iodide. In this medium, iodine is reasonably soluble as a consequence of the reaction

$$I_2(s) + I^- \rightleftharpoons I_3^- \qquad K = 7.1 \times 10^2$$

tri-iodide ion may be considered as a complex (sometimes also called the periodide ion). Thus, potassium iodide plays dual role, *viz., in iodimetry—to solubilize iodine in aqueous KI solution,* and in iodometry—as reducing agent, the excess KI helps in retaining liberated $I_2$ in solution through interaction with KI.

Iodine solutions lack stability for several reasons, one being the volatility of the solute. Losses of iodine from an open vessel occur in a relatively short time even in the presence of an excess of iodide ion. In addition, iodine slowly attacks most organic materials. Therefore, cork or rubber stoppers are never used to close containers of the reagent, and precautions must be taken to protect standard solutions from contact with organic dusts and fumes.

Hence, they cannot be used as primary standard solutions.

**Some Substances Determined by Iodimetry**

| Substance Determined | Reaction with Iodine | Solution Conditions |
|---|---|---|
| $H_2S$ | $H_2S + I_2 \rightarrow S + 2I^- + 2H^+$ | Acid solution |
| $SO_3^{2-}$ | $SO_3^{2-} + I_2 + H_2O \rightarrow SO_4^{2-} + 2I^- + 2H^+$ | |
| $Sn^{2+}$ | $Sn^{2+} + I_2 \rightarrow Sn^{4+} + 2I^-$ | Acid solution |
| As(III) | $H_2AsO_3^- + I_2 + H_2O \rightarrow HAsO_4^{2-} + 2I^- + 3H^+$ | pH 8 |
| $N_2H_4$ | $N_2H_4 + 2I_2 \rightarrow N_2 + 4H^+ + 4I^-$ | |

$$H_3AsO_3 + I_2 + H_2O \rightleftharpoons H_3AsO_4 + 2I^- + 2H^+$$

Iodine solutions can be standardized against anhydrous sodium thiosulfate or barium thiosulfate monohydrate, both of which are available commercially.

Aqueous solutions of tri-iodide ion $I_3^-$ exhibit a very sensitive yellow to brown color that is detectable by the human eye down to a concentration as lowas $5\times10^{-5}$ mol/L. The solution of $I_3^-$ may be its own indicator. During a direct iodometric titration, the equivalence point may be detected by the appearance of a persistent yellow color.

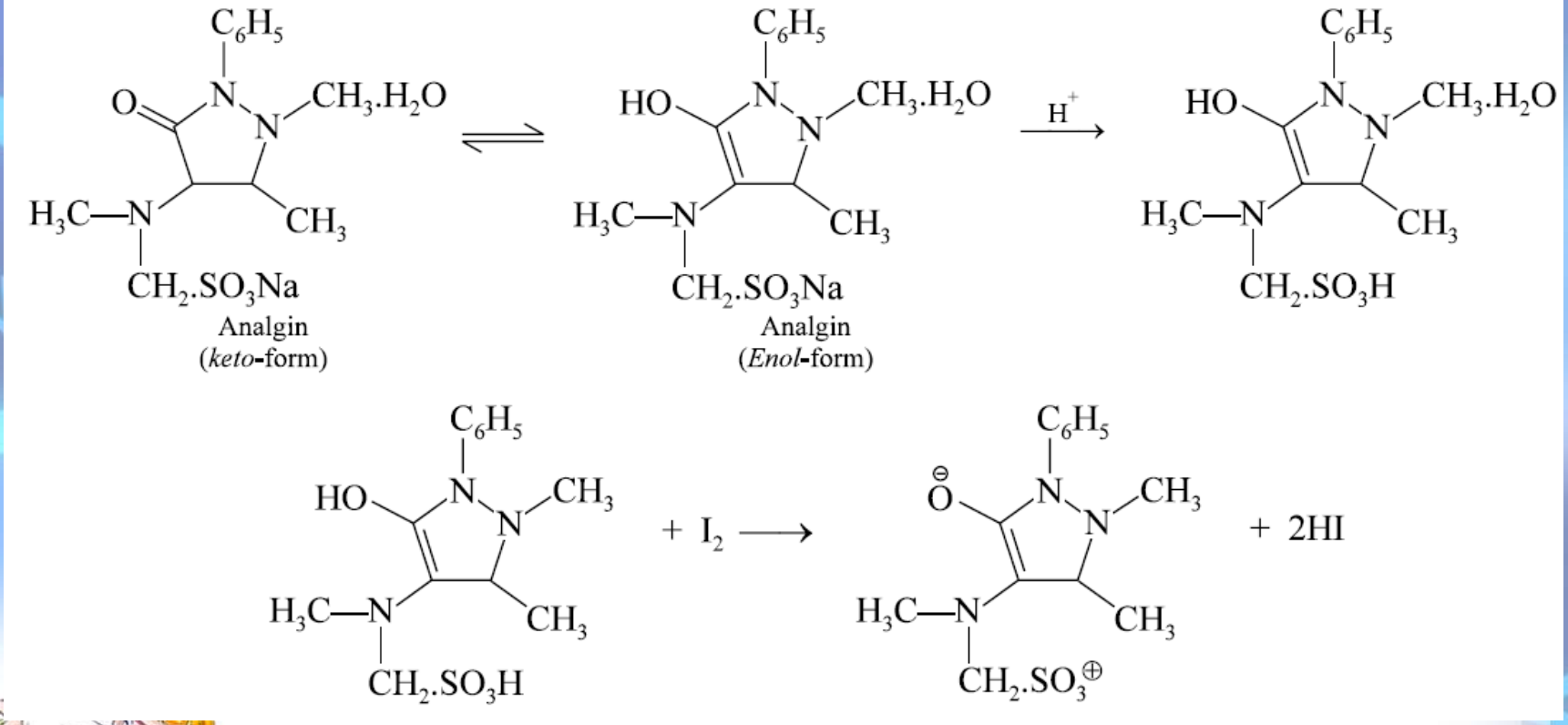
Another way to detect the equivalence point is to use starch as an indicator.

$$HCHO + I_2 + 3NaOH \rightarrow HCOONa + 2NaI + 2H_2O.$$

# Analgin

**Materials Required:** Analgin: 0.4 g; alcohol (95%):40 ml; 0.01N hydrochloric acid:10 ml; 0.1 N iodine solution.

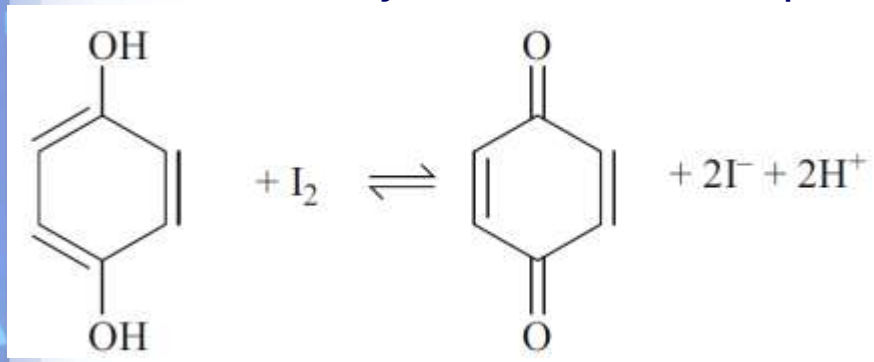
**Theory:** The estimation of analgin depends upon the oxidation of the enolic group with iodine. The reaction is not reversible:




**Procedure:** Weigh accurately about 0.4 g and dissolve in a mixture of 40 ml of alcohol and 10 ml of 0.01 N hydrochloric acid. Titrate the resulting mixture with 0.1 N iodine solution till a yellow colour that remains stable for 30 seconds is achieved.

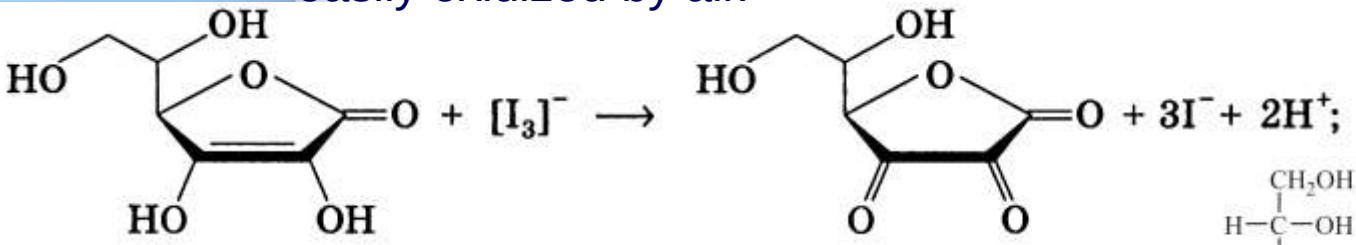
## Determination of Hydroquinol

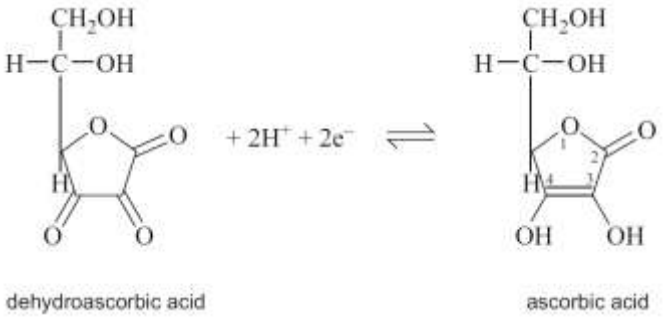
Iodine oxidizes hydroquinol into p-quinone in hydrogen carbonate medium. Actually, the reaction is equilibrated:




## Determination of Vitamin C

Through oxidization, vitamin C gives dehydroascorbic acid after the exchange of two electrons and two protons. The titration is achieved in acidic medium with an iodine solution as oxidant in the presence of starch. Ascorbic acid has been proposed as a reductant in some titrations. It is easily oxidized by air.




dehydroascorbic acid

ascorbic acid

# IODOMETRY

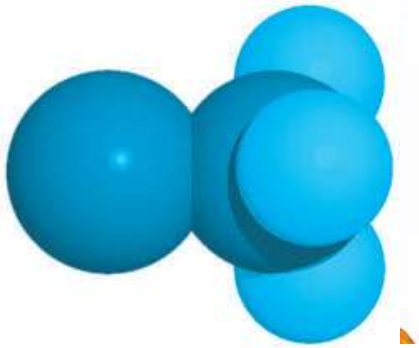
When an excess of iodide is added to a solution of an oxidizing agent, $I_2$ *is produced in an amount equivalent to the oxidizing agent present. This* $I_2$ *can, therefore,* be titrated with a reducing agent, and the result will be the same as if the oxidizing agent were titrated directly. The titrating agent used is sodium thiosulfate. Analysis of an oxidizing agent in this way is called an ***iodometric method*****.**

the two sulfur atoms of the disulfide bridge at oxidation state –I and the sulfur of the sulfonate groups at oxidation state +VI.

$$Cr_2O_7^{2-} + 6I^- \text{ (excess)} + 14H^+ \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O$$

The fundamental reaction of iodometries consists of the action of iodine or tri-iodide ions on thiosulfate ions $S_2O_3^{2-}$ giving tetrathionate ions $S_4O_6^{2-}$ according to the scheme

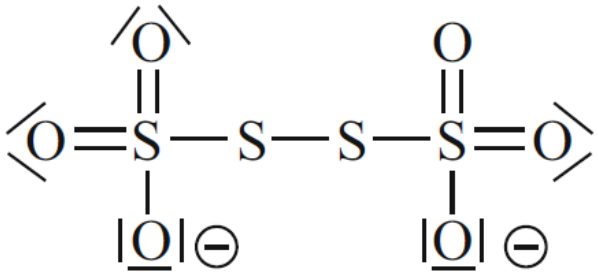
$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$



• The iodine/thiosulfate reaction can be used only in a slightly acidic medium, that is, in the approximate range 2< pH<5. In a strongly acidic medium (pH<2), thiosulfuric acid, which forms in these conditions, decomposes into sulfurous acid and sulfur according to the reactions

$$S_2O_3^{2-} + 2H^+ \rightarrow H_2S_2O_3$$

$$H_2S_2O_3 \rightarrow H_2SO_3 + S\downarrow$$



Thiosulfate ion ($S_2O_3^{2-}$) is a moderately strong reducing agent that has been widely used to determine oxidizing agents by an indirect procedure in which iodine is an intermediate.

## *Stability of Sodium Thiosulfate Solutions*

Although sodium thiosulfate solutions are resistant to air oxidation, they do tend to decompose to give sulfur and hydrogen sulfite ion. Variables that influence the rate of this reaction include pH, the presence of microorganisms, the concentration of the solution, the presence of copper(II) ions, and exposure to sunlight. These variables may cause the concentration of a thiosulfate solution to change by several percent over a period of a few weeks. Proper attention to detail will produce solutions that need only occasional restandardization. The rate of the decomposition reaction increases markedly as the solution becomes acidic.

The most important single cause for the instability of neutral or slightly basic thiosulfate solutions is bacteria that metabolize thiosulfate ion to sulfite and sulfate ions as well as to elemental sulfur. To minimize this problem, standard solutions of the reagent are prepared under reasonably sterile conditions. Bacterial activity appears to be at a minimum at a pH between 9 and 10, which accounts, at least in part, for the reagent's greater stability in slightly basic solutions. The presence of a bactericide, such as chloroform, sodium benzoate, or mercury(II) iodide, also slows decomposition.

Sodium thiosulfate, formerly called sodium hyposulfite or **hypo, is used to** "fix" photographic images and to extract silver from ore, as well as an antidote in cyanide poisoning, as a mordant in the dye industry, as a bleaching agent in a variety of applications, as the solute in the supersaturated solution of hot packs, and of course, as an analytical reducing agent. The action of thiosulfate as a photographic fixer is based on its capacity to form complexes with silver and thus dissolve unexposed silver bromide from the surface of photographic film and paper. Thiosulfate is often used as a dechlorinating agent to make aquarium water safe for fish and other aquatic life.

## Some Applications of Sodium Thiosulfate as a Reductant

| Analyte | Half-Reaction | Special Conditions |
|---|---|---|
| $IO_4^-$ | $IO_4^- + 8H^+ + 7e^- \rightleftharpoons \frac{1}{2}I_2 + 4H_2O$ | Acidic solution |
| | $IO_4^- + 2H^+ + 2e^- \rightleftharpoons IO_3^- + H_2O$ | Neutral solution |
| $IO_3^-$ | $IO_3^- + 6H^+ + 5e^- \rightleftharpoons \frac{1}{2}I_2 + 3H_2O$ | Strong acid |
| $BrO_3^-$, $ClO_3^-$ | $XO_3^- + 6H^+ + 6e^- \rightleftharpoons X^- + 3H_2O$ | Strong acid |
| $Br_2$, $Cl_2$ | $X_2 + 2I^- \rightleftharpoons I_2 + 2X^-$ | |
| $NO_2^-$ | $HNO_2 + H^+ + e^- \rightleftharpoons NO(g) + H_2O$ | |
| $Cu^{2+}$ | $Cu^{2+} + I^- + e^- \rightleftharpoons CuI(s)$ | |
| $O_2$ | $O_2 + 4Mn(OH)_2(s) + 2H_2O \rightleftharpoons 4Mn(OH)_3(s)$ | Basic solution |
| | $Mn(OH)_3(s) + 3H^+ + e^- \rightleftharpoons Mn^{2+} + 3H_2O$ | Acidic solution |
| $O_3$ | $O_3(g) + 2H^+ + 2e^- \rightleftharpoons O_2(g) + H_2O$ | |
| Organic peroxide | $ROOH + 2H^+ + 2e^- \rightleftharpoons ROH + H_2O$ | |

# Standardizing Thiosulfate Solutions

Potassium iodate is an excellent primary standard for thiosulfate solutions. In this application, weighed amounts of primary-standard-grade reagent are dissolved in water containing an excess of potassium iodide. When this mixture is acidified with a strong acid, the reaction

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

The liberated iodine is then titrated with the thiosulfate solution.

Other primary standards for sodium thiosulfate are potassium dichromate, potassium bromate, potassium hydrogen iodate, potassium hexacyanoferrate(III), and metallic copper. All these compounds liberate stoichiometric amounts of iodine when treated with excess potassium iodide.

The scheme used to determine oxidizing agents involves adding an unmeasured excess of potassium iodide to a slightly acidic solution of the analyte. Reduction of the analyte produces a stoichiometrically equivalent amount of iodine. The liberated iodine is then titrated with a standard solution of sodium thiosulfate, $Na_2S_2O_3$, one of the few reducing agents that is stable toward air oxidation.

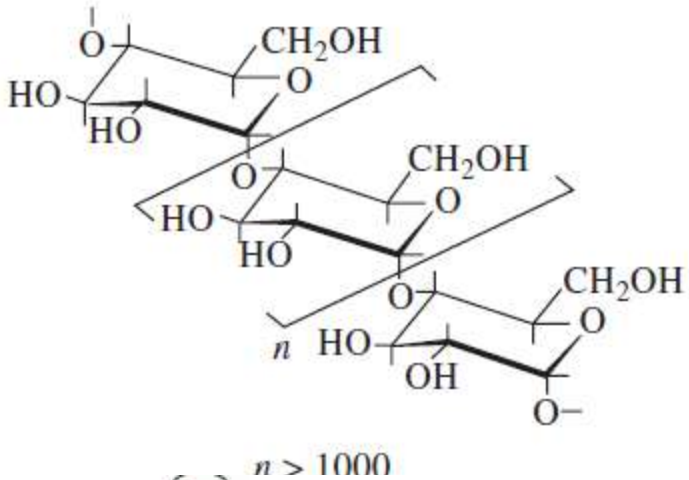
## Starch as an Indicators

Starch is often used in chemistry as an indicator for redox titration where triiodide is present. Starch forms a very dark blue-black complex with triiodide which can be made by mixing iodine with iodide (often from potassium iodide). However, the complex is not formed if only iodine ($I_2$) or only iodide ($I^-$) is present. The color of the starch complex is so deep, that it can be detected visually when the concentration of the iodine is as low as 0.00002 M at 20 °C.

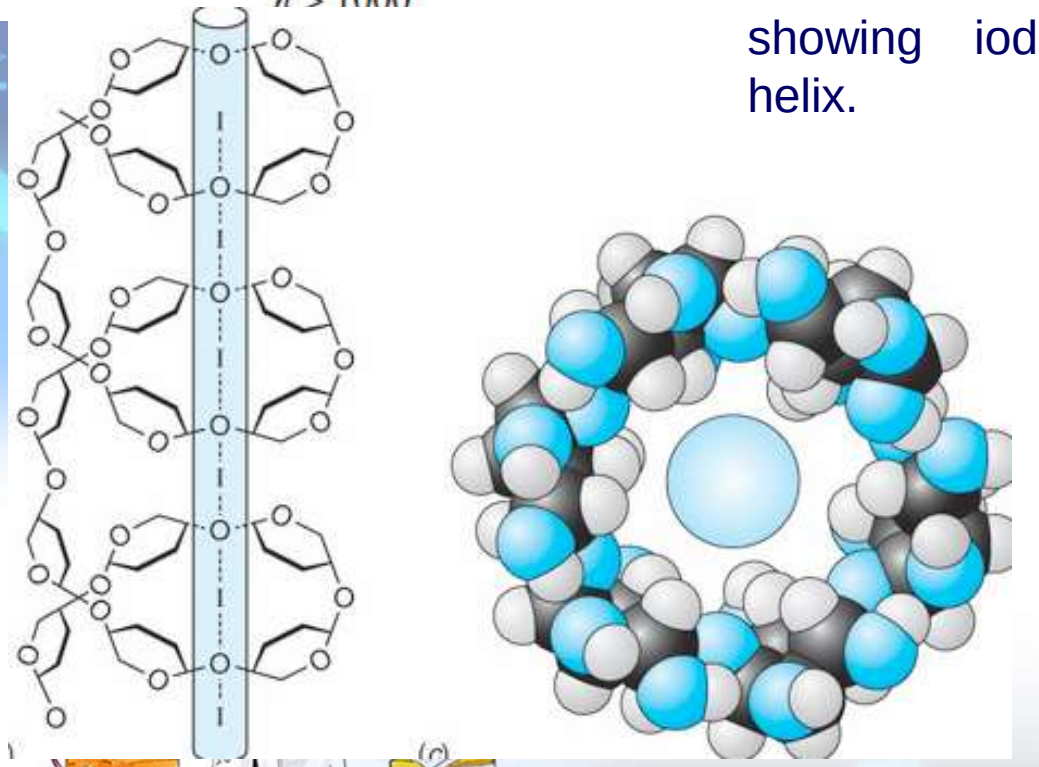
During iodine titrations, concentrated iodine solutions must be reacted with some titrant, often thiosulfate, in order to remove most of the iodine before the starch is added. This is due to the insolubility of the starch-iodine complex which may prevent some of the iodine reacting with the titrant. ***Close to the end-point***, the starch is added, and the titration process is resumed taking into account the amount of thiosulfate added before adding the starch.

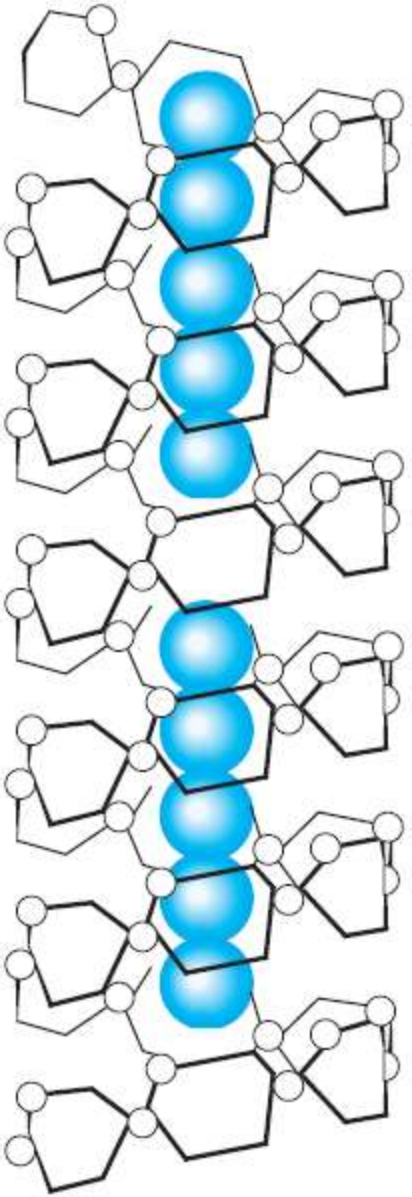
Starch is readily biodegraded, so it should be freshly dissolved or the solution should contain a preservative, such as $HgI_2$ (~1 mg/100 mL) or thymol. A hydrolysis product of starch is glucose, which is a reducing agent (partially hydrolyzed starch solution can be a source of error)

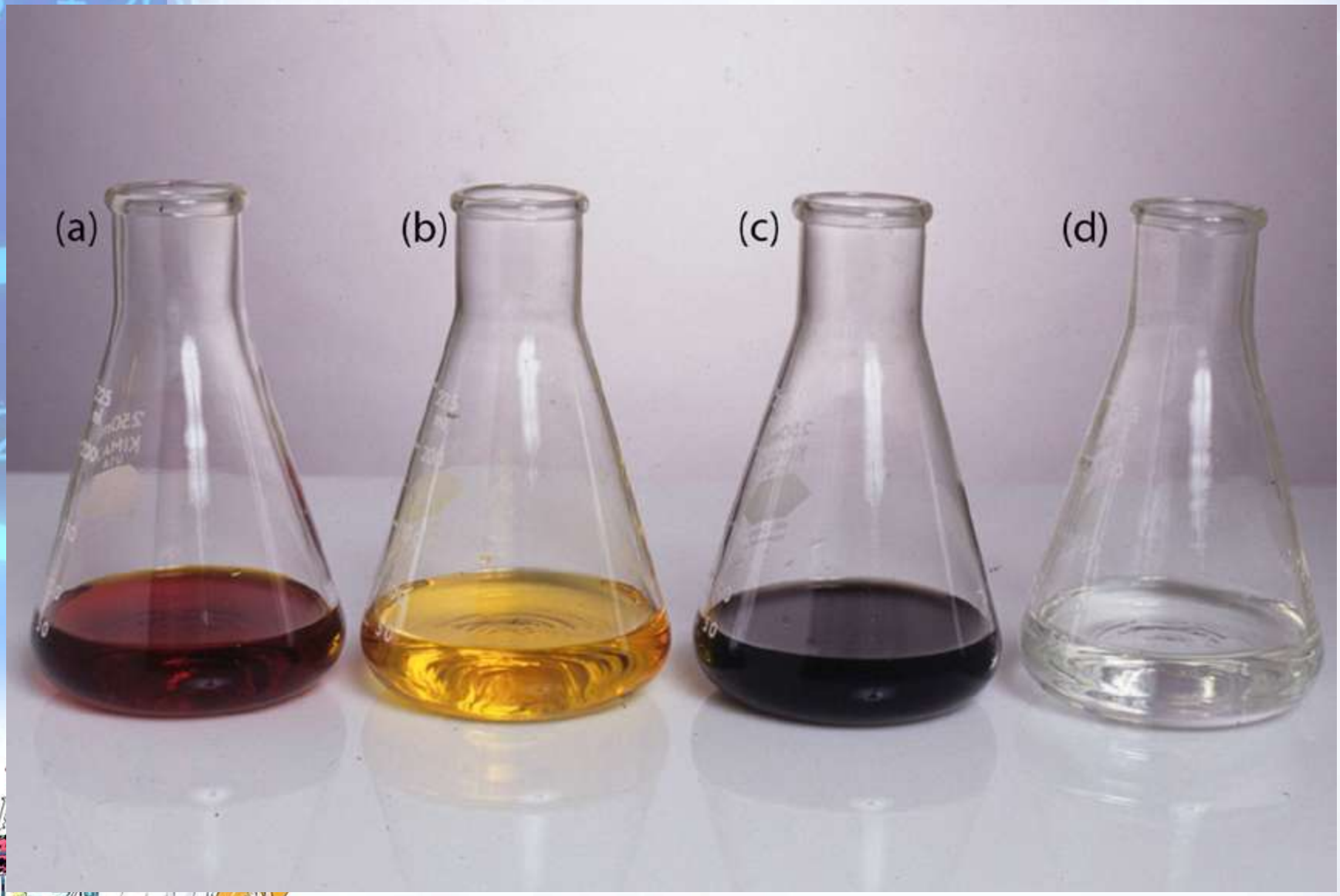
## Amylose (liaisonα-1,4-glucosyl)




Structure of the repeating unit of amylose (a polymer of the sugar α-D-glucose). (*b) Schematic structure of the starchiodine* complex. The amylose chain forms a helix around I6 units, which have a deep blue colour. (*c) View down the starch* helix, showing iodine inside the helix.






(a)
(b)
(c)
(d)

## Iodometric Determinations

| Substance Determined | Reaction with Iodide |
|---|---|
| $MnO_4^-$ | $2MnO_4^- + 10I^- + 16H^+ \rightleftharpoons 2Mn^{2+} + 5I_2 + 8H_2O$ |
| $Cr_2O_7^{2-}$ | $Cr_2O_7^{2-} + 6I^- + 14H^+ \rightleftharpoons 2Cr^{3+} + 3I_2 + 7H_2O$ |
| $IO_3^-$ | $IO_3^- + 5I^- + 6H^+ \rightleftharpoons 3I_2 + 3H_2O$ |
| $BrO_3^-$ | $BrO_3^- + 6I^- + 6H^+ \rightleftharpoons Br^- + 3I_2 + 3H_2O$ |
| $Ce^{4+}$ | $2Ce^{4+} + 2I^- \rightleftharpoons 2Ce^{3+} + I_2$ |
| $Fe^{3+}$ | $2Fe^{3+} + 2I^- \rightleftharpoons 2Fe^{2+} + I_2$ |
| $H_2O_2$ | $H_2O_2 + 2I^- + 2H^+ \xrightleftharpoons{\text{[Mo(VI) catalyst]}} 2H_2O + I_2$ |
| As(V) | $H_3AsO_4 + 2I^- + 2H^+ \rightleftharpoons H_3AsO_3 + I_2 + H_2O$ |
| $Cu^{2+}$ | $2Cu^{2+} + 4I^- \rightleftharpoons \underline{2CuI} + I_2$ |
| $HNO_2$ | $2HNO_2 + 2I^- \rightleftharpoons I_2 + 2NO + H_2O$ |
| $SeO_3^{2-}$ | $SeO_3^{2-} + 4I^- + 6H^+ \rightleftharpoons \underline{Se} + 2I_2 + 3H_2O$ |
| $O_3$ | $O_3 + 2I^- + 2H^+ \rightleftharpoons O_2 + I_2 + H_2O$ (can determine in presence of $O_2$ at pH 7–8.5) |
| $Cl_2$ | $Cl_2 + 2I^- \rightleftharpoons 2Cl^- + I_2$ |
| $Br_2$ | $Br_2 + 2I^- \rightleftharpoons 2Br^- + I_2$ |
| HClO | $HClO + 2I^- + H^+ \rightleftharpoons Cl^- + I_2 + H_2O$ |

# Determining Water with the Karl Fischer Reagent

In industry and commerce, one of the most widely used analytical methods is the Karl Fischer titration procedure for the determination of water in various types of solids and organic liquids. This important titrimetric method is based on an oxidation/ reduction reaction that is relatively specific for water.

The Karl Fischer reaction is based on the oxidation of sulfur dioxide by iodine. In a solvent that is neither acidic nor basic—an aprotic solvent—the reaction can be summarized by

$$I_2 + SO_2 + 2H_2O \rightarrow 2HI + H_2SO_4$$

In this reaction, two moles of water are consumed for each mole of iodine. The stoichiometry, however, can vary from 2:1 to 1:1 depending on the presence of acids and bases in the solution.

In order to stabilize the stoichiometry and shift the equilibrium further to the right, Fischer added pyridine ($C_5H_5N$) and used anhydrous methanol as the solvent. A large excess of pyridine was used to complex the $I_2$ and $SO_2$. The classic reaction has been shown to occur in two steps. In the first step, $I_2$ and $SO_2$ react in the presence of pyridine and water to form pyridinium sulfite and pyridinium iodide.

$$C_5H_5N \cdot I_2 + C_5H_5N \cdot SO_2 + C_5H_5N + H_2O \rightarrow 2C_5H_5N \cdot HI + C_5H_5N \cdot SO_3$$

$$C_5H_5N^+ \cdot SO_3^- + CH_3OH \rightarrow C_5H_5N(H)SO_4CH_3$$

This second step is important because the pyridinium sulfite can also consume water:

$$C_5H_5N^+ \cdot SO_3^- + H_2O \rightarrow C_5H_5NH^+SO_4H^-$$

1. Solvolysis $2ROH + SO_2 \rightleftharpoons RSO_3^- + ROH_2^+$
2. Buffering $B + RSO_3^- + ROH_2^+ \rightleftharpoons BH^+SO_3R^- + ROH$
3. Redox $B \cdot I_2 + BH^+SO_3R^- + B + H_2O \rightleftharpoons BH^+SO_4R^- + 2BH^+I^-$

Note that the stoichiometry is again one mole of $I_2$ consumed for each mole of $H_2O$ resent in the sample.

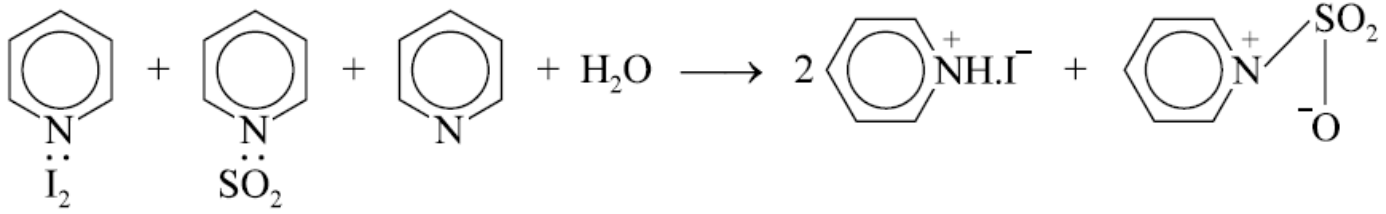
For volumetric analysis, the classical Karl Fischer reagent consists of $I_2$, $SO_2$, pyridine, and anhydrous methanol or another suitable solvent. The reagent decomposes on standing and must be standardized often.

***Detecting the End Point***

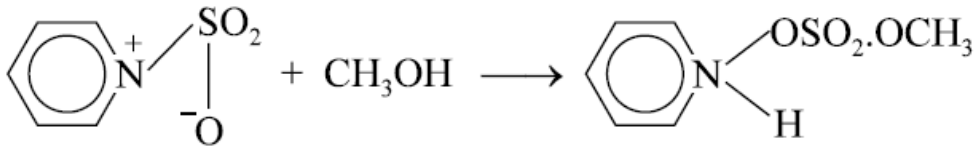
An end point in a Karl Fischer titration can be observed visually based on the brown color of the excess reagent. More commonly, however, end points are obtained by electroanalytical measurements.

Water present in the analyte reacts with the Karl Fischer reagent in a two-stage process as shown below:

**Stage 1 :**




**Stage 2 :**

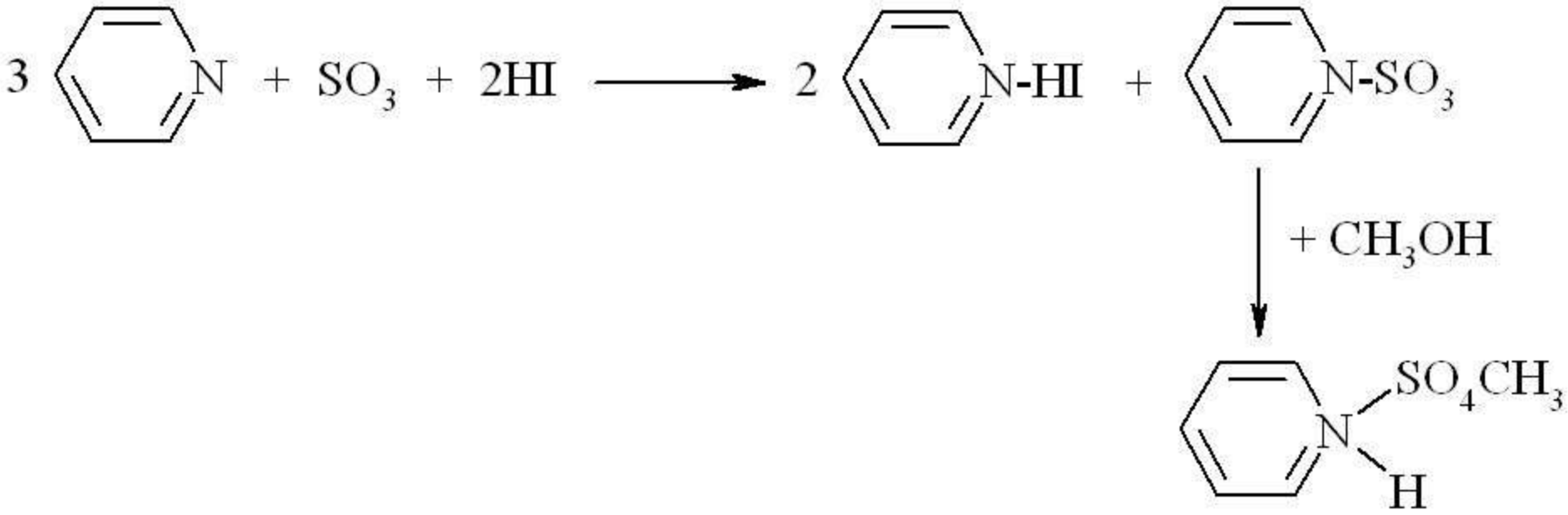



From Eq. (*a) step I, it is obvious that the oxidation of sulphur dioxide takes place by iodine to yield* sulphur trioxide and hydrogen iodide thereby consuming one mole of water. In other words, each one molecule of iodine disappears against each molecule of water present in the given sample. It is pertinent to mention here that in the presence of a large excess of pyridine ($C_5H_5N$), all reactants as well as the resulting products of reaction mostly exist as complexes as evident from Eqs. (*a) and (b).*

# Determination of moisture content (Karl-Fischer reagent)

- **Reagent**: $I_2 + SO_2$ + anhyd. $CH_3OH$ and anhyd. pyridine.
- Sample containing moisture + reagent until appearance of yellow color of the xss iodine.

$$SO_2 + I_2 + H_2O \rightarrow SO_3 + 2HI$$



## APPLICATIONS OF KARL FISCHER METHOD FOR DETERMINATION OF WATER IN PHARMACEUTICAL ANALYSIS

The Karl Fischer method for the determination of water is used for prednisolone sodium phosphate, Rifamycin Sodium, Sodium Methyl Hydroxybenzoate, Triamcinolone Acetonide as described below.

**Materials Required:** Karl Fischer Reagent: 100 ml; prednisolone sodium phosphate: 0.2 g; anhydrous methanol: 20.0 ml.

**Procedure:** Add about 20 ml of anhydrous methanol to the titration vessel and titrate to the amperometric end-point with the Karl Fischer reagent. Quickly add 0.2 g of prednisolone sodium phosphate sample, stir for 1 minute and again titrate to the amperometric end-point with the Karl Fischer reagent. The difference between the two titrations gives the volume (*v) of Karl Fischer reagent consumed by the sample.* The minimum water equivalent is 3.5 mg of water per ml of Karl Fischer reagent. Hence, the percentage of water w/w in the given sample may be calculated by the following expression:

$$\text{Water \% (w/w)} = \frac{v \times 3.5}{\text{wt. of sample (mg)}} \times 100$$

**Precautions**

(1) The reagents and solutions used must be kept anhydrous and necessary care should be taken throughout to prevent exposure to atmospheric moisture,

(2) The Karl Fischer reagent should be protected from light and preferably stored in a bottle fitted with an automatic burette, and

(3) The water equivalent of Karl Fischer reagent should always be determined before use.

# Determination of Hypochlorites

Most of the time, hypochlorites are determined by indirect iodometry. These determinations are of great practical interest since, for example, bleaching chlorides (calcium hypochlorite) and bleaching solutions (sodium hypochlorite) are determined in such a manner. Chlorine is used industrially for its oxidizing, bleaching, and antiseptic properties, among others. Its use is difficult and dangerous.

$$2Ca(OH)_2 + 2Cl_{2(g)} \rightarrow Ca(ClO)_2 + CaCl_2 + 2H_2O.$$

$$HClO + Cl^- + H^+ \rightarrow H_2O + Cl_2,$$

Hypochlorite ions decompose in acidic medium and liberate chlorine in the presence of chlorides. This fact leads to the concepts of active chlorine and *chlorometric degrees*.This equivalence is the origin of the concept of ***active chlorine***. *We notice* that active chlorine truly evolves only when the decomposition of the hypochlorite takes place in hydrochloric acid medium. The *chlorometric degree* is the number of liters of gaseous chlorine evolved in normal conditions that may be released by one liter of hypochlorite solution or by one kilogram of product in the presence of hydrogen chloride.

$$ClO^- + 2I^- + 2H^+ \rightarrow Cl^- + I_2 + H_2O.$$

**Theory :** Chlorinated lime reacts with acetic acid to produce a mole each of calcium acetate, hydrochloric acid and hydrochlorous acid. The two acids interact to give water and chlorine, and the latter reacts with HI to liberate iodine that can be estimated by titrating with 0.1 N sodium thiosulphate solution. The various reactions involved may be expressed as given below :

$$CaCl(OCl) + 2CH_3COOH \longrightarrow Ca(CH_3COO)_2 + HCl + HClO$$

$$HCl + HClO \longrightarrow H_2O + Cl_2$$

$$2HI + Cl_2 \longrightarrow 2HCl + I_2$$

**Procedure :** Weigh accurately 4.0 g of chlorinated lime and triturate it in a glass-pestle-mortar with a little DW. Transfer the paste quantitatively into a 1 litre volumetric flask and shake thoroughly. Take a 100 ml volumetric flask, rinse it with a small quantity of the suspension from the 1 litre flask and finally fill it up with the suspension. Rinse out a 250 ml iodine flask containing a little dilute acetic acid and a little of the suspension from the 1-litre flask in order to oxidise any inorganic substance present in the iodine flask. Finally, wash it thoroughly with DW. Now, transfer 100 ml of the suspension completely from the 100 ml volumetric flask to the iodine flask by washing the former repeatedly with DW. Add to it acetic acid 5 ml followed by KI 3.0 g and shake the contents of the flask thoroughly. Titrate the liberated iodine with 0.1 N sodium thiosulphate which is equivalent to 0.003546 g of chlorine. From this value the percentage of chlorine present in the given sample of chlorinated lime can be calculated.

# Cupric Ions

Cupric ions oxidize iodide ions according to the equation

$$2Cu^{2+} + 4I^- \rightarrow 2CuI_{(s)} + I_2.$$

The liberated iodine is titrated with thiosulfate.

This is not a simple redox reaction. There is also a precipitation reaction together with the redox one. Half of the iodide ions added are indeed oxidized into iodine, while the other half remains at state –I. The part that the latter plays is to precipitate Cu+I as cuprous iodide. Cu+I is formed by the redox reaction between $Cu^{2+}$ and $I^-$:

$$2Cu^{2+} + 2I^- \rightarrow 2Cu^+ + I_2,$$

$$Cu^+ + I^- \rightarrow CuI_{(s)}.$$

The precipitation of cuprous as cuprous iodide permits its stabilization. The cuprous ions that are not precipitated (or complexed) do not exist in aqueous solution. They disproportionate according to

$$2Cu^+ \rightleftharpoons Cu^{2+} + Cu_{(s)}, \quad K^\circ = 5.4 \cdot 10^5 \text{ at } 25\ ^\circ C.$$

$$I_2 + 2Cu^+ \rightarrow 2Cu^{2+} + 2I^- \quad Cu^{2+} + 1e^- + I^- \rightleftharpoons CuI_{(s)},$$

The $Cu^{2+}/I^-$ reaction is the basis of several methods of the determination of reducing sugars. They are based on the reducing properties of these sugars, due to the presence of an aldehyde or an enediol function in their structure.

# CHLORIODOMETRY

## Titrant iodine monochloride ICl

When potassium iodate is used as an oxidising agent in the presence of an excess of concentrated hydrochloric acid, the reduction product is iodine monochloride, where iodine is formally in the +1 oxidation state.

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

$$IO_3^- + 4e + 6H^+ \longrightarrow I^+ + 3H_2O$$


**Materials Required:** Potassium iodide -0.5; hydrochloric acid (11.5 N) -35 ml; chloroform: 5 ml; 0.05 M potassium iodate.

**Procedure:** Weigh accurately 0.5 g of potassium iodide and dissolve it in about 10 ml of DW. Add to it 35 ml of hydrochloric acid and 5 ml of chloroform. Titrate with 0.05 M potassium iodate till the purple colour of iodine disappears from the chloroform layer. Add the last portion of the iodate solution carefully and dropwise while shaking the contents of the flask vigorously and continuously. Allow to stand for 5 minutes. In case any colour still develops in the chloroform layer continue the titration.

This reaction has been used for the determination of many reducing agents.

## Standardization of ICl

$$ICl + KI\,(excess) \rightarrow I_2 + KCl$$

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

$$\overset{+1}{ICl} + 2\bar{e} \rightarrow \overset{-1}{I^-} + Cl^- \qquad E^0_{ICl/I^-} = +0.80\ B$$

**At the equivalence point:**

$$ICl + I^- \rightarrow I_2 + Cl^-$$

Condition of titration: **pH ≤ 7**

$$I_2 + starch \rightarrow blue\ compound$$

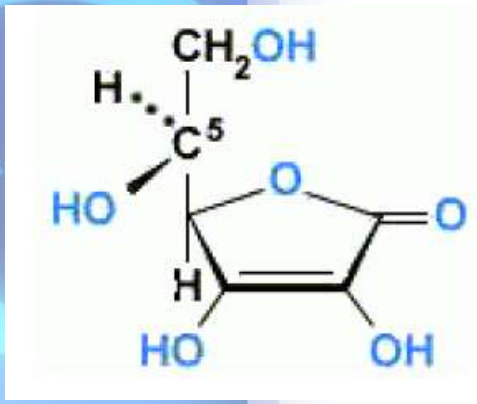
## Determination of $SnCl_2$ (direct titration)

$$SnCl_2 + ICl + 3HCl \rightarrow HI + H_2[SnCl_6]$$

$$HI + ICl \rightarrow I_2 + HCl$$

$$I_2 + starch \rightarrow blue\ compound$$

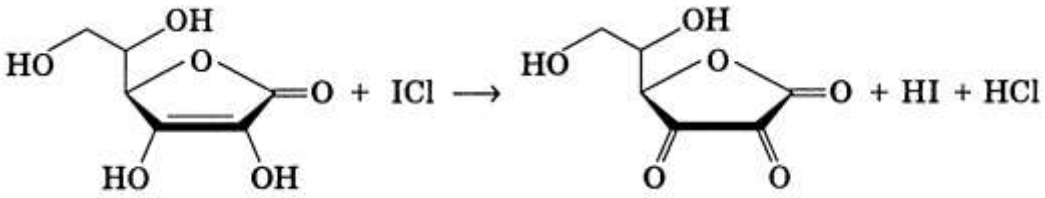
## Determination of Vit C

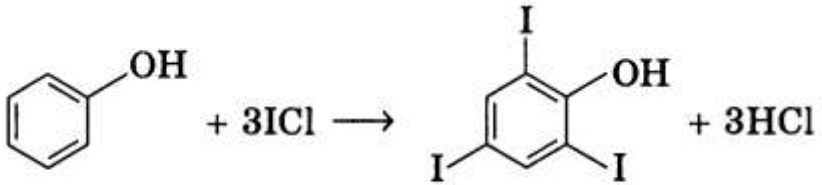


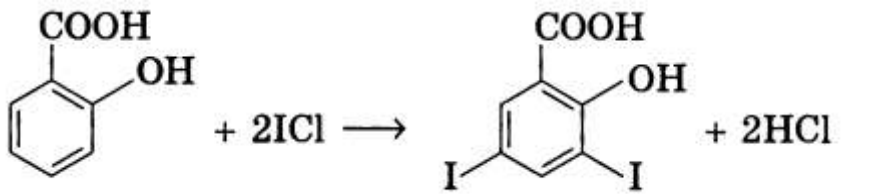

$$C_6H_8O_6 + ICl \rightarrow C_6H_6O_6 + HI + HCl$$

$$HI + ICl \rightarrow I_2 + HCl$$

$$I_2 + starch \rightarrow blue\ compound$$



## Determination of mercury (I) salts (back titration)

$$2Hg_2Cl_2 + 2ICl\,(excess) \rightarrow HgI_2 \downarrow + 3HgCl_2 + ICl\,(leftover)$$

$$KI\,(excess) + ICl\,(leftover) \rightarrow I_2 + KCl$$

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

**Advantages of the method:**

**1.The solution of ICl is more stable, than solution of iodine.**

**2.This method can be applied for the determination of more reducing agents as well as organic compounds.**

# IODATOMETRIC TITRATION titrant sol. $KIO_3$

The term “iodatometry” groups titration methods involving potassium iodate as the oxidant. Potassium iodate is available in at least a 99.9% state of purity. Before use in iodatometry, it must be dried at 120°C. The anhydrous salt does not tend to absorb the ambient moisture. It is a good primary standard.

Potassium iodate is a powerful oxidizing agent, but the course of the reaction is governed by the conditions under which it is employed.
The reaction between potassium iodate and reducing agent in solutions of moderate acidity (0,1-2 M HCl) stops at the stage when iodate is reduced to iodine.

$$IO_3^- + 5e^- + 6H^+ \rightleftharpoons I_2 + 3H_2O, \quad E^\circ(IO_3^-/I_2) = 1.18\,V$$

With a more powerful reductant the iodate is reduced to iodide:

$$IO_3^- + 6e^- + 6H^+ \rightleftharpoons I^- + 3H_2O, \quad E^\circ(IO_3^-/I^-) = 1.09\,V.$$

In more strongly acid solution (3-6 M HCl) reduction occurs to iodine monochloride, and it is under these conditions that is most widely used.

$$IO_3^- + 6H^+ + 2Cl^- + 4e^- \rightleftharpoons ICl_2^- + 3H_2O, \quad E^\circ(IO_3^-/ICl_2^-) = 1.24\,V.$$

These reactions has been used for the determination of many reducing agents.

## Determination of $SnCl_2$

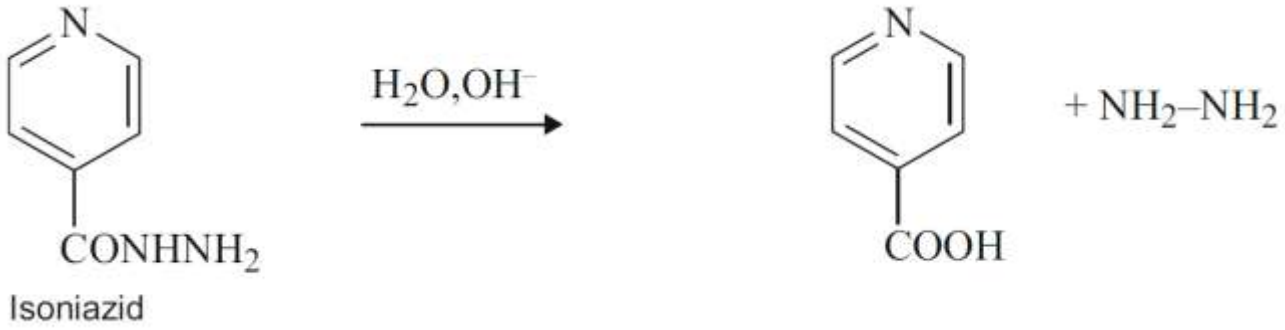
$$3SnCl_2 + 3KIO_3 + 12HCl \rightarrow KI + 3H_2[SnCl_6] + 3H_2O$$

$$KIO_3 + 5KI\,(excess) + 6HCl = 3I_2 + 6KCl + 3H_2O$$

## Determination of hydrazine

$$IO_3^- + N_2H_5^+ + H^+ + Cl^- \rightarrow ICl + N_{2(g)} + 3H_2O.$$

The titration of isoniazid or isonicotinic acid hydrazid, a pharmaceutical of great interest, is based on this titration reaction:




Isoniazid

In a first step, isoniazid is quantitatively hydrolyzed to give isonicotinic acid and hydrazine, which is titrated by the iodatometry.

## Determination of KBr

$$10KBr + 2KIO_3(excess) + 12HCl \rightarrow 5Br_2 \uparrow + I_2 \uparrow + 12KCl + 6H_2O + KIO_3(leftover)$$

$$KIO_3(leftover) + 5KI(excess) + 6HCl = 3I_2 + 6KCl + 3H_2O$$

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

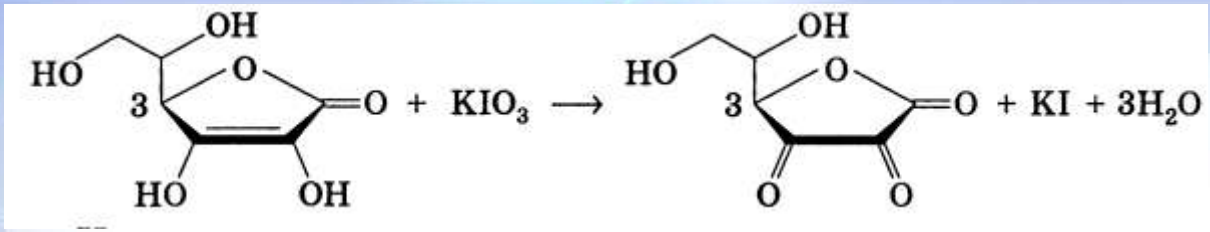
## Determination of KI

In the initial stage 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.

$$KIO_3 + 2KI + 6HCl = 3ICl + 3KCl + 3H_2O$$

$$ICl + KI = KCl + I_2$$

$$I_2 + KIO_3 + 6HCl = 5ICl + KCl + 3H_2O$$


OH
HO
O
3
O
HO
OH
+ KIO3
OH
HO
O
3
O
O
O
+ KI + 3H2O