KARL FISCHER TITRATION

(For determination of moisture content)

- Karl Fischer proposed a reagent which reacts quantitatively & selectively with water to measure a moisture content.

- Karl Fischer reagent consist of iodine,SO_2 in a mixture of anhydrous pyridine & anhydrous methanol

- Recently pyridine has been replaced by other amines particularly imidazole

- It involves a quantitative reaction of water with iodine and SO_2 in the presence of lower alcohol such as methanol & organic base such as pyridine

$$H_2O + I_2 + SO_2 + 3C_6H_5N \longrightarrow 3C_6H_5NH^+I^- + C_6H_5N\text{-}SO_3$$

(Pyridinium iodide) (Pyridinium sulphide)

Reaction of iodine and SO_2 in the presence of pyridine and water forms pyridinum sulphide and pyridinium iodide.

In this method water react with iodine in quantitative amt which means that 1 mole of iodine react with 1 mole of water

-Reaction of pyridinium sulphide with methanol gives a complex.

These are 2 methods for the determination of moisture content

i) Volumetric method

ii) Coulometric method

(Depending upon the iodine provided)

Volumetric Method

In this method iodine required for reaction with water is previously dissolved in the water determination test standard (Karl Fischer reagent) & water content is determined by measuring the amount of iodine consume as a result of reaction with water in a sample.

-two methods of titration can be done to determine the end point of the reaction

i) Amperiometric method- at constant voltage(change in current is measured)

ii) Potentiometric method – at constant current(change in potential is measured)

Procedure for Karl Fischer

- Direct method

- Back titration method

Direct method

i) Take 25 ml of methanol for water determination in a dried titration flask& titrate with water determination test standard to the end point

ii) Weigh accurately a quantity of sample(usually containing 10 to 50 mg of water) & transfer it quickly into titration flask & dissolve by stirring

iii) Titrate the solution with water determination test standard to the end point under rigorous stirring.

Calculation

Water (moisture) present= $\frac{\text{Vol (ml) of KF reagent X f (mg / ml) X100}}{\text{wt of sample(mg)}}$

F = no of mg of water of water correspondence to 1 ml of water determination test standard(need specific amt of Karl Fisher reagent)which reacts with specific amount of water.

- This is specific for different sample.

2**) Back titration method**

- Take 25 ml of methanol for water determination in dried titration flask & titrate with water determination test standard to the end point.

- Weigh accurately suitable quantity of sample & transfer the sample to titration vessel.

- Add an excess of and definite volume of water determination test standard

- Stir the content for 30 minutes protecting from atmospheric moisture.

- Titrate the solution with water methanol standard solution from the burette.

Calculation

Water(moisture) present= (Vol of Karl Fischer reagent) X f - Volume of water-methanol solution consumed) f^1 X 100 / wt of sample

f^1= no of mg of water in 1 ml of water methanol standard solution

Caulometric Method

In this method , iodide are used instead of iodine & the time consumed in formation of iodine from iodide can be measured.

- In this , Karl Fischer reagent contain potassium iodide instead of iodine

- In this titration first iodine is produced by electrolysis of reagent containing iodide ion & then the water content in a sample is determined by measuring the quantity of electricity which is required for production of iodine.

- The titration shall consist of aniodic & cathodic compartment separated by ceramic layer(diaphragm)

- The anionic compartment contain analyte solution which include SO_2,KI & pyridine needed for chemical reaction , methanol or ethanol is used as solvent.

-In coulometric Karl Fischer titration when iodine is complete & the amt of water in sample is calculated by measuring the current needed for electrochemical generation of iodine from iodide.

- If ceramic layer is absent , the change of iodine is reversed , hence the diaphragm plays an role in titration cell.

Anodic reaction = $2I^- \text{----------} I_2 + 2\ e^-$

Cathodic reaction = $I_2 \text{----------} I_2 + 2\ e^- \text{----------} 2I$

Iodine is a decolorizer which give sharp increase in a current.

<u>Interfering Reaction of Karl Fischer Titration</u>

-Karl Fischer water determination is only specific ,if no side reaction takes place with Karl Fischer reagent.

- this means that no water should be released in side reaction& the sample react with any of the component of a reagent.

Some of the interfering reactions are summarized below

-Carboxyl grp(aldehyde & ketones)- Aldehyde & Ketones can react with sulphurdioxide & water & water to form bisulphate complex .

Aldehyde & ketones can combine with methanol in Karl Fischer reagent to form acetols and ketols

<u>Prevention</u>

Using methanol free Karl Fischer reagent or replacing methanol by higher alcohol

Eg- 2 –methoxy methanol

-By making use of different reaction rate & slowing down acetols and ketols formation [by carrying out titration at -10^oC]