GRAVIMETRIC TITRATIONS

Q.   Write a note on Ignition.

Ans. When temperature used is below 250^0C, the process is known as drying which can carried out in electric drying oven. When temperature above 250^0C to 1200^0C is used the process is referred to as Ignition which is carried out in Muffle furnace. In gravimetric procedure, separated substance must be converted to a form which is suitable for weighing i.e. should be pure, stable, should have definite composition. Ignition at higher temperature is required for complete removal of water that is occluded or very strongly adsorbed and for complete conversion to desired compound. Eg. Ignition of CaC_2O_4 to CaO, chemical change requires high temperature.

Errors: Incomplete removal of water, volatile electrolytes, reduction of precipitates by carbon when filter paper is employed.
 Crucible should be properly covered and kept in desiccators as they cool.

Q.   0.4852 g sample of iron ore is dissolved in acid and iron is oxidized to the +3 state and then precipitated as hydrous oxide, $Fe_2O_3. xH_2O$. The ppt. is filtered, washed & ignited to Fe_2O_3 which is found to be 0.2481 g. Calculate the % of iron in sample.

Ans. $2Fe^{3+}$ --------- $Fe_2O_3.x H_2O$ --------- Fe_2O_3 (S)
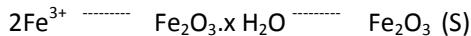
Since 2 mol of Fe^{3+} produce 1 mol of Fe_2O_3

Gravimetric Factor: = 2 FW of Fe / FW of Fe_2O_3 = 2 x 55.85/159.69 = 0.6994
        (FW= Formula weight)

$$\%A \quad = \frac{w.o\ a}{w.o\ sc} \times G.F. \times 100$$

% of Fe = wt. of analyte x G.F. x100/ wt. of sample
        = 0.2481 x 0.6994 x 100 / 0.4852 = 35.76%

➢ Separation processes should be sufficiently complete so that quantity of analyte left un-precipitated is 0.1 mg or even less.
➢ Substance weighed should have definite composition and should be pure.
➢ Precipitate formed should be filterable.

Q.   Calculate the gravimetric factors of following:

a) P in Ag_3PO_4 atomic wt. of P= 30.97, FW of Ag_3PO_4 : 711.22

mmol of P   =   mmol of Ag_3PO_4

or GF $= \frac{m\ P}{3.9} = \frac{m\ A\ 3P\ 4}{7.2} = \frac{m\ P}{m\ A\ 3P\ 4} = \frac{3.9}{7.2} = 0.04354$

a)   Fe in Fe_2O_3 2 moles of Fe in Fe_2O_3

GF $= \frac{2x F\ o\ 2F}{F\ o\ F\ 2O3}$

b)   Fe in Fe_3O_3 3 moles of Fe in Fe_3O_3

$$GF = \frac{F\ o\ 3F}{F\ o\ F\ 3O3} = 55.85 \times 3 = 167.55 + 48 = 215/ \quad 167.55/215 = 0.779$$

c) MgO in $Mg_2P_2O_7$ 2 MgO
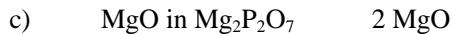
$$GF = \frac{F\ o\ 2M}{F\ o\ M\ 2P2O7}$$

Q. Describe the process of incineration.

Ans. Silica crucible is ignited to a constant weight (with in 0.0002 g) at which the precipitate is to be heated. Packet of precipitate is placed in crucible. Place the crucible on pipe clay silica triangle on a ring stand. Incline the crucible, half covered, introduce flame slowly increase flame. Carbonize the paper. Paper should not be put to flames or else small particles of precipitate during combustion may be lost. It takes about 20 minutes to char the paper and 30 to 60 minutes for complete ignition. After 1-2 min crucible & lid are kept in the dessicator . Cool the crucible for 25-30 min.; weigh the crucible & lid. Crucible & lid are again ignited at same temp for 10-20 min.; repeat same procedure till a constant weight is obtained. Empty crucible & lid are also subjected to same procedure.

$$Fe(HCO)_3 \cdot nH_2O(s) \xrightarrow[1\ hr]{850°C} Fe_2O_3(s)\ +\ xCO_2\uparrow\ +\ yH_2O\uparrow$$

Q. Write the applications of Gravimetric analysis.

Ans. 1) To determine the purity & thermal stability of both primary & secondary standards.

2) Investigation of correct drying temperature & suitability of various weighing forms for gravimetric analysis.

3) Direct application to analytical problems. (automatic thermogravimetric analysis)

4) To determine composition of complex mixtures.

5) To assess the purity of materials. Eg. Cement, moisture & ash determination of food & agriculture products, polymers, rubbers, ceramics.

Q. Discuss the determination of Barium as Barium sulphate.

Ans. This is widely used method. Solubility of Barium sulphate is 1 parts in 400000 of cold water or about 2.5 mg/ml. Solubility in hot water is greater or in dilute hydrochloric acid or nitric acid and less in solutions containing common ion. Barium is precipitated by sulphuric acid or from homogenous solution by the use of suphamic acid solution which produces sulphate on boiling.

$$NH_2SO_3H \ + \ H_2O \ \rightleftharpoons \ NH_4^+ \ + \ SO_4^{\ 2-} \ + \ H^+$$

Procedure: With H_2SO_4 acid: Solution (100ml) should contain not more than 1% by volume of conc. HCl. Heat to boiling, add a slight excess of hot $0.5M\text{-}H_2SO_4$ slowly & with stirring. Digest on steam bath until precipitate has settled, filter, wash with hot water containing two drops of H_2SO_4/lit. & then with little water until the acid is removed. Filter, wash, ignite (900-1000^0C), weigh as $BaSO_4$.

Suphate as $BaSO_4$: Dilute solution of BaCl2 is added to hot solution of sulfate slightly acidified with HCl adding slowly.

$$Ba^{++} \ + SO_4^{\ 2-} \ \longrightarrow \ BaSO_4$$

Precipitates are filtered, washed with water, ignited at red hot & weighed as $BaSO_4$