D.N.R.COLLEGE (AUTONOMOUS): BHIMAVARAM
DEPARTMENT OF PG CHEMISTRY

APPLIED ANALYSIS – II

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UNIT-I

ANALYSIS OF RAW MATERIALS

Sampling:-

Sampling is the process of collection of small portion from the bulk material. This represents the entire characteristics of the bulk material. These are two methods.

Method-I: - Cone and Quartering Method :-(Diagram)

Here bulk sample arranged in a cone shape. Now we can remove the top of the cone, we get a flattened shape. Then it is divided into four parts, the alternative parts are taken in to the top of cone add and then repeating the process 3 (or) 4 times. Finally we get a representative sample parts. This is representing the entire characteristics of bulk materials.

Method -II:-Long pile Alternative Shovel Method :-(Diagram)

Here bulk sample arranged in a long pile (or) Path. Then its cuts in to a several parts, opposite parts are again converted in to long pile and also then it cuts into several parts are taken to this add remaining parts of the first long pile. Then it is again converted in to long pile. The process is repeating the 3 (or) 4 times. Finally we get a representative sample.

Dissolution:-

Dissolve the sample in a suitable amount of diluted HNO_3 (1:1) and applying and boiling until evaporate the reddish brown vapors are evolved out and it is cooled, filter the solution, filtrate is used for the determination of copper (Cu), zinc (Zn), lead (Pb). Residue contains Meta stannic acid (H_2SnO_3) it is used for the determination of tin (Sn).

a) Analysis of non-ferrous alloys:-

i) & ii) Analysis of Brass & Bronze:-

The following constituents are present in the brass & bronze:

Determination of Copper

Determination of Zinc

Determination of Tin

Determination of Lead

Determination of Iron

Determination of Alumina

Determination of Nickel

Determination of Antimony (Sb)

Determination of Arsenium (As)

Determination of Phosphorous

Determination of Manganese

The major constituents are present in the brass and bronze are Cu, Zn, Sn, Pb, and Fe.

The minor constituents are present in the brass and bronze are P, Al, Sb, As, Mn, Ni Etc...

The amount of major constituents present in brass & bronze are following:

	Brass	**Bronze**
Cu	60-90%	60-90%
Zn	1.5-40%	<25%
Sn	0-6%	35%
Pb	0-2%	<25%
Fe	0-3%	<25%

Determination of Tin (Sn):-

Accurately weighed 1g of sample is taken into a 250mL beaker. Give the sample contain over 1.5% of tin (Sn). Then to this added 15mL of diluted HNO_3 and then this solution is boiled, until reddish brown vapours are evolved out. After then this solution is cooled and placed in a water bath. After Then to this added 50mL of water and then this solution is digest for half an hour, filter the solution, filtrate is removed. It is used for the determination of Cu, Zn, Pb. The residue contains phosphorous, and then it is washed with diluted HNO_3. After then residue is taken and it contains Meta stannic acid. Then this solution is heated and cooled. After then it is converted in to SnO_2.Finally weighed as SnO_2 precipitate.

$$\% \, SnO_2 = \frac{\text{Weight of the } SnO_2 \times 0.7877}{\text{Total weight of the sample}} \times 100$$

Determination of Lead in Bronze:-

We take the filtrate from the tin (Sn) determination. After then to this added 10mL of concentrated H_2SO_4. Until evaporated the solution, then white fumes are completely evolved out. Then the solution is cooled for few min and then filters the solution. Filtrate is taken in to a Gooch crucible and then it is heated strongly. It is cooled in desiccators, finally weighed as a $PbSO_4$.

$$\% \, PbSO_4 = \frac{\text{Weight of the } PbSO_4 \times 0.6833}{\text{Total weight of the sample}} \times 100$$

Determination of Copper & Lead:-

Determination of Lead in Brass & Copper in Brass & Bronze:-

Electrolysis method:-

Dilute the filtrate from the tin (Sn) determination and then to this added approximately 200mL of concentrated HNO_3. The solution contains then to this added 10% of 10mL of concentrated H_2SO_4 is approximately. Electrolyte the solution in a beaker, starting with a current of 2 amps & gradually working up to 3 amp. In the blue colour of the solution is disappear, using either a rotating anode (or) rotating cathode and continuous the electrolysis for 45min at the end of this time stop the rotation of the electrode but do not turn of the electrolysis current. Lower the beaker & switch of the current just before the electrodes come out of the solution quickly wash the electrodes with distilled water from a wash bottle. Remove and immerse immediately in methyl alcohol. Then burn of the alcohol in the air keeping the electrodes in constant motion cool in desiccators and weighed. The cathode contains copper in the metallic state and anode contains the Lead as Lead oxide. Calculate the later to lead. Test the solution for complete removal of copper and lead by electrolysis with fresh electrodes. The difference is the weights of electrodes represent the amount of copper and lead percentage present in the sample.

$$\% \text{ Lead} = \frac{\text{Weight of } PbO_2 \text{ X } 0.8643}{\text{Total weight of the sample X } 100}$$

Determination of Zinc by Zinc-Phosphate method:-

The determination of zinc is done by electrolysis method (or) zinc-phosphate method. Filtrate from the removal of copper and lead. The iron and alumina precipitate are hydroxide by the addition of excess of NH_4OH.filter the solution. Filtrate is used for the determination of zinc.

We take the filtrate and then to this added 1mL of concentrated HCl and excess amount of 10% of NH_3 or Sodium phosphate. After then this solution is heat to boiling and then added to NH_4OH rapidly, until all the precipitate is re dissolves and then slowly acidified with acetic acid, stir the solution, until the precipitate becomes crystal ion. After then this solution is stands for several hours. After then solution is filter. The crystals are Gooch crucible is taken and wash with hot water and then it is heated strongly. Finally Weighed as $Zn_2P_2O_7$ precipitate.

$$\% \text{ Zinc} = \frac{\text{Weight of the } Zn_2P_2O_7 \text{ X } 0.4290}{\text{Total weight of the sample}} \text{ X } 100$$

Determination of Iron & Alumina in Brass & Bronze:-

Filtrate is taken from the removal of copper & lead determination. It is used for the determination of Iron & Alumina. Then it is acidified with concentrated HCl and alkaline with NaOH. After then to this added excess amount of NH_4OH. We get a precipitate as iron & alumina. After then it is taken into a Gooch crucible and heated and cooled. Then it is fused with potassium bisulphate, then added sufficient amount of 5% of H_2SO_4. After then this solution is titrated with $KMnO_4$.Then to calculate the Iron. The weight from the total weight of iron & alumina, finally we get alumina.

$$\% \text{ Iron} = \frac{\text{Volume of } KMnO_4 \text{ X } 0.0056}{\text{Total weight of the sample X } 100}$$

Weight of Alumina = Total weight of iron & alumina-Weight of iron

$$\% \text{ Alumina} = \frac{\text{Weight of the } Al_2O_3 \text{ X } 0.5291}{\text{Total weight of the sample}} \text{ X } 100$$

Determination of Nickel:-

Filtrate is obtained, after then removal of copper & lead. After then this solution is used for the nickel determination. After then to this added 5mL of concentrated H_2SO_4 and then evaporate the solution, until white fumes are completely evolved out. After then it is heated in a Gooch crucible. After then to this added quickly pour the 50% 30mL of NaOH. After then we get a Nickel hydroxide precipitate. After then it is heated in a Gooch crucible & then it is cooled in a desiccators. Then Weighed as Nickel oxide precipitate.

$$\% \text{ Nickel} = \frac{\text{Weight of the Nickel Oxide X } 0.7858}{\text{Total weight of the sample}} \text{ X } 100$$

Determination of Antimony (Sb):-

Accurately weighed 3-10g of sample is taken into an Erlenmeyer flask. After then to this added 30mL of concentrated HNO_3 & then to this added sufficient amount of pure tin (Sn) (3:1) ratio. After then solution is evaporated up to 10mL. After then to this added 250mL of hot water, then we get a precipitate. Then precipitate is not formed. Then the solution is taken into an asbestos flask. It is worked as a cathode. It is used for the removal of copper present in the solution. After then to this added 15mL of concentrated H_2SO_4 & 5-10g of potassium sulphate (K_2SO_4) & then to this added sufficient amount of 10% of tartaric acid. After then this solution is heated & cooled, then to this added few ml of concentrated HCl. After then this solution is titrated with $KMnO_4$.

$$\% \text{ Antimony} = \frac{0.5100}{\text{Volume of } KMnO_4}$$

Determination of Arsenic (As):-

Accurately weighed 3-10g of sample is taken into a Kjeldahl flask. Then to this added $FeCl_3$, it is used for dissolving purpose & then it is diluted slowly. Then the distillation a solution is taken into a one lit Erlenmeyer flask, after distillation is completed. Then the solution is neutralized with NaOH & acidified with HCl & alkaline with $NaHCO_3$.Then to this added few drops of starch as indictor. Then it is titrated with iodine solution.

$$\% \text{ Arsenic} = \frac{0.007575}{\text{Volume of Iodine}}$$

Determination of Phosphorous:-

It is determined by two methods

1) Gravimetric method:-

Principle:-

It is present in the sample it is oxidized by addition of 3 (or) 4mL of Nitric acid solution for the sample and then added to the sufficient amount of AmmoniumMolybdate and then it is heated. Finally we get an Ammonium PhosphoMolybdate.

$$(NH_3)_4PO_412MoO_4\text{+Excess }NaOH \rightarrow Na_2MoO_3+Na_2HPO_4+NH_3+H_2O$$

Chemicals required: - HNO_3, AmmoniumMolybdate.

Apparatus: - Platinum crucible, Desicator.

Procedure:-

Accurately weighed 5 g of sample is taken in to a Platinum crucible. After then it is treated with HNO_3 & Ammonium Molybdate and then it is heated and then we get an Ammonium PhosphoMolybdate. Finally collated in a desiccators and then it is dried and then weighed as Ammonium Phospho Molybdate.

$$\% \text{ Phosphorous} = \frac{0.378 \text{ X Weight of Ammonium PhosphoMolybdate.}}{\text{Total weight of the sample}} \text{ X } 100$$

2) Volumetric method:-

Accurately weighed 5g of sample is taken in to a Platinum crucible. After then it is treated with HNO_3 & Ammonium Molybdate.

After then it is heated and then we get Ammonium PhosphoMolybdate. After then to this added excess amount of NaOH solution. The untreated NaOH is titrated with HCL by using a Phenolphthalein indicator.

$$\text{Untreated } NaOH + HCl \rightarrow NaCl + H_2O$$

Factor: - 1mL of 0.1N NaOH = 0.003088g of P_2O_5

Determination of Manganese:-

It can be determined by two methods

1) Gravimetric method:-

Principle:-

Filtrate is taken, after then removal of Al, Fe, and Cr. Then to this added sufficient amount of Bromine water and NH_4OH and then we get a hydrated Manganese Oxide precipitate and then finally it is ignited and then we get a Mn_3O_4.

$$Filtrate+Br_2+NH_4OH \rightarrow Mn_2O_2H_2O \rightarrow Mn_3O_4$$

Chemicals required: - Bromine water, Ammonium Hydroxide

Apparatus: - Platinum crucible, Dessicator.

Procedure:-

Filtrate obtained, after removal of Al, Cr, and Fe. After then to this added sufficient amount of Br_2&NH_4OH and then we get a Hydrated MnO_2H_2O precipitate. Filter the precipitate and then used for the analysis. Residue is taken in to a Platinum crucible. After then it is heated at 50-72^{0}c and then we get a Mn_3O_4. Finally it is cooled in a dessicator and then dried and then finally weighed as Mn_3O_4.

$$\% \text{ Manganese} = \frac{\text{Weight of } Mn_3O_4 \text{ X } 0.7203}{\text{Total weight of the sample}} \text{ X } 100$$

2) Volumetric method:-

Filtrate obtained, after removal of Al, Fe, and Cr. After then it is heated with H_2SO_4 and then we get a $MnSO_4$. After then to this added few ml of HNO_3 and then to firm a clear solution, the clear solution is titrated with $KMnO_4$.

Factor: - 1mL of 0.1N $KMnO_4$ = 0.001648g of Manganese

iii) Analysis of solder:-

The following constituents are:

Determination of Tin (Sn)

Determination of Lead (Pb)

Determination of Antimony (Sb)

Determination of Tin (Sn):-

Accurately weighed 5-10g of sample is taken into a 250mL beaker. Then it is dissolved in 2:1 HNO_3. Then it is heated and then reddish brown vapours are evolved out completely. Filter the precipitate; residue is washed with 2% HNO_3 as to remove the phosphorous. Then the residue is taken into a platinum crucible and then heated and cooled in desiccators & finally weighed as SnO_2, PbO_2, and Sb_2O_4. After then to this added one part of precipitate to the 3 parts of sulphur & sodium carbonate & also added excess amount of Na_2SO_3. Then convert into any poly sulphates to mono sulphates. It indicates the total weight of Sn, As, Sb, PbO_2. Let it consider as a later “a”. Lead can be calculated by electrolysis (or) gravimetric method. Let it can be consider a “b”. Antimony can be calculated by volumetric method. Let it can be consider as “c”. Here calculate the tin (Sn).

% Tin (Sn) = a- (b + c)

b) Analysis of Ferro alloys:-

i) Analysis of Ferro silicon:-

The following constituents are:

Determination of Silica

Determination of Carbon

Determination of Phosphorous

Determination of Sulphur

Determination of Silica:-

Accurately weighed 5g of sample is taken into a platinum crucible. After then it is dissolved in sufficient amount of HCl solution, after then it is treated with fusing mixture. Then we get a fused mass. After then it is heated with 1:1 HCl at 500^{0}C for 15min. After then cooled in a desiccators, then precipitate is formed, filter the precipitate, then to form a residue. Then loss of weight of the sample formed.

Residue is taken & then to this added 1 (or) 2 ml of concentrated H_2SO_4 and few ml of HF solution is added. Then to form a SiF_4.Finally weighed as a residue solution.

$$SiO_2+4HF \rightarrow SiF_4+2H_2O$$

$$\% \text{ Silica} = \frac{\text{Loss of weight of the sample}}{\text{Total weight of the sample}} \text{ X } 100$$

Determination of Carbon:-

Accurately weighed 5g sample is taken into a procaine crucible (porcelain crucible). Then it is placed at heating chamber contains free weighed KOH tube and another end passing through the dry air. Then sample is heated at 110^{0}c. Then CO_2 is observes in a KOH tube. Then increase the KOH tube weight. Finally KOH tube weighed.

$$\% \text{ Carbon} = \frac{\text{Increase KOH tube Weight X } 0.2727}{\text{Total weight of the sample}} \text{ X } 100$$

Determination of Phosphorous:-

It is determined by two methods

1) Gravimetric method:-

Principle:-

It is present in the sample, it is oxidized by addition of 3 (or) 4mL of Nitric acid solution for the sample and then added to the sufficient amount of Ammonium Molybdate and then it is heated. Finally we get an Ammonium PhosphoMolybdate.

$$(NH_3)_4PO_412MoO_4\text{+Excess }NaOH \rightarrow Na_2MoO_3+Na_2HPO_4+NH_3+H_2O$$

Chemicals required: - HNO_3, Ammonium Molybdate.

Apparatus: - Platinum crucible, Desiccators.

Procedure:-

Accurately weighed 5 g of sample is taken in to a Platinum crucible. After then it is treated with HNO_3 & Ammonium Molybdate and then it is heated and then we get an Ammonium Phospho Molybdate. Finally collated in a desiccators and then it is dried and weighed as Ammonium Phospho Molybdate.

$$\% \text{ Phosphorous} = \frac{0.378 \text{ X Weight of Ammonium Phospho Molybdate}}{\text{Total weight of the sample}} \text{ X } 100$$

2) Volumetric method:-

Accurately weighed 5g of sample is taken in to a Platinum crucible. After then it is treated with HNO_3 and Ammonium Molybdate. After then it is heated and then we get Ammonium Phospho Molybdate. After then to this added excess amount of NaOH solution. The untreated NaOH is titrated with HCl by using a Phenolphthalein indicator.

$$\text{Untreated } NaOH + HCl \rightarrow NaCl + H_2O$$

Factor: - 1mL of 0.1N NaOH = 0.003088g of P_2O_5

Determination of Sulphur:-

Principle:-

In this determination of sulphur is converted in to sulphates by the adding of fusing mixture in the sample solution. After then it is treated with HCl and $BaCl_2$ solution and then we get a $BaSO_4$ precipitate.

$$SO_4^{-2}+HCl+BaCl \rightarrow BaSO_4$$

Chemicals required: - Fusing mixture, HCl, $BaCl_2$

Apparatus: - Platinum crucible, desiccators

Procedure:-

Accurately weight 5g of sample taken in to a platinum crucible. After then it is treated with fusing mixture. Then we get a fused mass. After then it is dissolved in water and we get a sulphate. After then it is treated with HCl and $BaCl_2$ and then we get a $BaSO_4$.

$$\% \text{ Sulphur} = \frac{0.1374 \text{ X Weight of } BaSO_4}{\text{Total weight of the sample}} \text{ X } 100$$

ii) Analysis of Ferro Vanadium:-

The following constituents are:

Determination of Vanadium

Determination of Carbon

Determination of Phosphorous

Determination of Sulphur

Determination of Silica

Determination of Alumina

Determination of Vanadium:-

Principle:-

In this determination of vanadium & then to this added excess amount of iron solution. Then it is converted in to V (V) to V (IV). Then untreated Fe (II) is titrated with $KMnO_4$ solution.

$$V (V) + Fe (II) \rightarrow V (IV) + Fe (III)$$

$$Fe (II) + Mn (VII) \rightarrow Fe (III) + Mn (II)$$

Procedure:-

Accurately weighed 5g of sample is taken into a 250mL beaker. Then it is dissolved in sufficient amount of H_2SO_4 solution from the above solution. Then we take 20ml of sample is taken into a 250mL conical Flask. After then to this added excess amount of Fe (II) solution. Then we get vanadium, then untreated Fe (II) solution is titrated with $KMnO_4$ solution, finally we get a Fe (III).

$$\% \text{ Vanadium} = \frac{(AXB)\ XCX0.05095}{\text{Total weight of the sample X 100}}$$

Here,
A = Volume of $KMnO_4$ is required for the titration
B = Volume of $KMnO_4$ is required for the back titration
C = Concentration of $KMnO_4$ solution

Determination of Carbon:-

Accurately weighed 5g sample is taken into a procaine crucible (porcelain crucible). Then it is placed at heating chamber contains free weighed KOH tube and another end passing through the dry air. Then sample is heated at 110^0c. Then CO_2 is observes in a KOH tube. Then increase the KOH tube weight. Finally KOH tube weighed.

$$\% \text{ Carbon} = \frac{\text{Increase KOH tube Weight X 0.2727}}{\text{Total weight of the sample}} \text{ X 100}$$

Determination of Phosphorous:-

It is determined by two methods

1) Gravimetric method:-

Principle:-

It is present in the sample, it is oxidized by addition of 3 (or) 4mL of Nitric acid solution for the sample and then added to the sufficient amount of Ammonium Molybdate and then it is heated. Finally we get an Ammonium PhosphoMolybdate.

$$(NH_3)_4PO_412MoO_4 + \text{Excess } NaOH \rightarrow Na_2MoO_3 + Na_2HPO_4 + NH_3 + H_2O$$

Chemicals required: - HNO_3, Ammonium Molybdate.

Apparatus: - Platinum crucible, Desiccators.

Procedure:-

Accurately weighed 5 g of sample is taken in to a Platinum crucible. After then it is treated with HNO_3 & Ammonium Molybdate and then it is heated and then we get an Ammonium Phospho Molybdate. Finally collated in a desiccators and then it is dried and weighed as Ammonium Phospho Molybdate.

$$\% \text{ Phosphorous} = \frac{0.378 \text{ X Weight of Ammonium Phospho Molybdate}}{\text{Total weight of the sample}} \text{ X } 100$$

2) Volumetric method:-

Accurately weighed 5g of sample is taken in to a Platinum crucible. After then it is treated with HNO_3 and Ammonium Molybdate. After then it is heated and then we get Ammonium Phospho Molybdate. After then to this added excess amount of NaOH solution. The untreated NaOH is titrated with HCl by using a Phenolphthalein indicator.

$$\text{Untreated } NaOH + HCl \rightarrow NaCl + H_2O$$

Factor: - 1mL of 0.1N NaOH = 0.003088g of P_2O_5

Determination of Sulphur:-

Principle:-

In this determination of sulphur is converted in to sulphates by the adding of fusing mixture in the sample solution. After then it is treated with HCl and $BaCl_2$ solution and then we get a $BaSO_4$ precipitate.

$$SO_4^{-2} + HCl + BaCl \rightarrow BaSO_4$$

Chemicals required: - Fusing mixture, HCl, $BaCl_2$

Apparatus: - Platinum crucible, desiccators

Procedure:-

Accurately weight 5g of sample taken in to a platinum crucible. After then it is treated with fusing mixture. Then we get a fused mass. After then it is dissolved in water and we get a sulphate. After then it is treated with HCl and $BaCl_2$ and then we get a $BaSO_4$.

$$\% \text{ Sulphur} = \frac{0.1374 \text{ X Weight of } BaSO_4}{\text{Total weight of the sample}} \text{ X } 100$$

Determination of Silica:-

Accurately weighed 5g of sample is taken in to a platinum crucible. After then it is dissolved in sufficient amount of HCl solution. After then it is treated with fusing mixture and then to produced fused mass. After then it is heated with 1:1 HCl at 500^0c for 15min. Then it is cooled in desiccators. Precipitate is formed and then filter the precipitate and then to form a residue. Here loss of weight of the sample solution.

$$\% \text{ Silica} = \frac{\text{Loss of weight of the sample}}{\text{Total weight of the sample}} \times 100$$

Determination of Alumina:-

Accurately weighed 5g of the sample is taken into a platinum crucible. After then it is treated with HNO_3 and 3(or) 4mL of NH_4OH. Then to form an Al $(OH)_3$ precipitate. Filter the precipitate, residue is taken, then it is treated with HCl solution. After then to this added Na_2PO_4 (or) $(NH_4)_2PO_4$. We get an $AlPO_4$ precipitate. Then it is washed with suitable solvent. Then it is ignited & dried & finally Al_2O_3 is formed.

$$\% \text{ Alumina} = \frac{\text{Weight of the } Al_2O_3 \times 0.4178}{\text{Total weight of the sample}} \times 100$$

iii) Analysis of Ferro Manganese:-

The following constituents are:

Determination of Manganese

Determination of Sulphur

Determination of Carbon

Determination of Phosphorous

Determination of Silica

Determination of Manganese:-

It can be determined by two methods

1) Gravimetric method:-

Principle:-

Filtrate is taken, after then removal of Al, Fe, and Cr. Then to this added sufficient amount of Bromine water and NH_4OH and then we get a hydrated Manganese Oxide precipitate and then finally it is ignited and then we get a Mn_3O_4.

$$\text{Filtrate} + Br_2 + NH_4OH \rightarrow Mn_2O_2H_2O \rightarrow Mn_3O_4$$

Chemicals required: - Bromine water, Ammonium Hydroxide

Apparatus: - Platinum crucible, Dessicator.

Procedure:-

Filtrate obtained, after removal of Al, Cr, and Fe. After then to this added sufficient amount of Br_2&NH_4OH and then we get a Hydrated MnO_2H_2O precipitate. Filter the precipitate and then used for the analysis. Residue is taken in to a Platinum crucible. After then it is heated at $50\text{-}72^0$c and then we get a Mn_3O_4. Finally it is cooled in a dessicator and then dried and then finally weighed as Mn_3O_4.

$$\% \text{ Manganese} = \frac{\text{Weight of } Mn_3O_4 \times 0.7203}{\text{Total weight of the sample}} \times 100$$

2) Volumetric method:-

Filtrate obtained, after removal of Al, Fe, and Cr. After then it is heated with H_2SO_4 and then we get a $MnSO_4$. After then to this added few ml of HNO_3 and then to firm a clear solution, the clear solution is titrated with $KMnO_4$.

Factor: - 1mL of 0.1N $KMnO_4$ = 0.001648g of Manganese

Determination of Sulphur:-

Principle:-

In this determination of sulphur is converted in to sulphates by the adding of fusing mixture in the sample solution. After then it is treated with HCl and $BaCl_2$ solution and then we get a $BaSO_4$ precipitate.

$$SO_4^{-2}+HCl+BaCl\rightarrow BaSO_4$$

Chemicals required: - Fusing mixture, HCl, $BaCl_2$

Apparatus: - Platinum crucible, desiccators

Procedure:-

Accurately weight 5g of sample taken in to a platinum crucible. After then it is treated with fusing mixture. Then we get a fused mass. After then it is dissolved in water and we get a sulphate. After then it is treated with HCl and $BaCl_2$ and then we get a $BaSO_4$.

$$\% \text{ Sulphur} = \frac{0.1374 \text{ X Weight of } BaSO_4}{\text{Total weight of the sample}} \text{ X } 100$$

Determination of Carbon:-

Accurately weighed 5g sample is taken into a procaine crucible (porcelain crucible). Then it is placed at heating chamber contains free weighed KOH tube and another end passing through the dry air. Then sample is heated at 110^0c. Then CO_2 is observes in a KOH tube. Then increase the KOH tube weight. Finally KOH tube weighed.

$$\% \text{ Carbon} = \frac{\text{Increase KOH tube Weight X } 0.2727}{\text{Total weight of the sample}} \text{ X } 100$$

Determination of Phosphorous:-

It is determined by two methods

1) Gravimetric method:-

Principle:-

It is present in the sample, it is oxidized by addition of 3 (or) 4mL of Nitric acid solution for the sample and then added to the sufficient amount of Ammonium Molybdate and then it is heated. Finally we get an Ammonium PhosphoMolybdate.

$$(NH_3)_4PO_412MoO_4+\text{Excess } NaOH\rightarrow Na_2MoO_3+Na_2HPO_4+NH_3+H_2O$$

Chemicals required: - HNO_3, Ammonium Molybdate.

Apparatus: - Platinum crucible, Desiccators.

Procedure:-

Accurately weighed 5 g of sample is taken in to a Platinum crucible. After then it is treated with HNO_3 & Ammonium Molybdate and then it is heated and then we get an Ammonium Phospho Molybdate. Finally collated in a desiccators and then it is dried and weighed as Ammonium Phospho Molybdate.

$$\% \text{ Phosphorous} = \frac{0.378 \times \text{Weight of Ammonium Phospho Molybdate}}{\text{Total weight of the sample}} \times 100$$

2) Volumetric method:-

Accurately weighed 5g of sample is taken in to a Platinum crucible. After then it is treated with HNO_3 and Ammonium Molybdate. After then it is heated and then we get Ammonium Phospho Molybdate. After then to this added excess amount of NaOH solution. The untreated NaOH is titrated with HCl by using a Phenolphthalein indicator.

$$\text{Untreated NaOH} + HCl \rightarrow NaCl + H_2O$$

Factor: - 1mL of 0.1N NaOH = 0.003088g of P_2O_5

Determination of Silica:-

Accurately weighed 5g of sample is taken in to a platinum crucible. After then it is dissolved in sufficient amount of HCl solution. After then it is treated with fusing mixture and then to produced fused mass. After then it is heated with 1:1 HCl at 500^0c for 15min. Then it is cooled in desiccators. Precipitate is formed and then filter the precipitate and then to form a residue. Here loss of weight of the sample solution.

$$\% \text{ Silica} = \frac{\text{Loss of weight of the sample}}{\text{Total weight of the sample}} \times 100$$

iv) Analysis of Silico Manganese:-

The following constituents are:

Determination of Manganese

Determination of Sulphur

Determination of Carbon

Determination of Phosphorous

Determination of Silica

Determination of Manganese:-

It can be determined by two methods

1) Gravimetric method:-

Principle:-

Filtrate is taken, after then removal of Al, Fe, and Cr. Then to this added sufficient amount of Bromine water and NH_4OH and then we get a hydrated Manganese Oxide precipitate and then finally it is ignited and then we get a Mn_3O_4.

$$Filtrate+Br_2+NH_4OH \rightarrow Mn_2O_2H_2O \rightarrow Mn_3O_4$$

Chemicals required: - Bromine water, Ammonium Hydroxide

Apparatus: - Platinum crucible, Dessicator.

Procedure:-

Filtrate obtained, after removal of Al, Cr, and Fe. After then to this added sufficient amount of Br_2&NH_4OH and then we get a Hydrated MnO_2H_2O precipitate. Filter the precipitate and then used for the analysis. Residue is taken in to a Platinum crucible. After then it is heated at 50-72^{0}c and then we get a Mn_3O_4. Finally it is cooled in a desiccators and then dried and then finally weighed as Mn_3O_4.

$$\% \text{ Manganese} = \frac{\text{Weight of } Mn_3O_4 \text{ X } 0.7203}{\text{Total weight of the sample}} \text{ X } 100$$

2) Volumetric method:-

Filtrate obtained, after removal of Al, Fe, and Cr. After then it is heated with H_2SO_4 and then we get a $MnSO_4$. After then to this added few ml of HNO_3 and then to firm a clear solution, the clear solution is titrated with $KMnO_4$.

Factor: - 1mL of 0.1N $KMnO_4$ = 0.001648g of Manganese

Determination of Sulphur:-

Principle:-

In this determination of sulphur is converted in to sulphates by the adding of fusing mixture in the sample solution. After then it is treated with HCl and $BaCl_2$ solution and then we get a $BaSO_4$ precipitate.

$$SO_4^{-2}+HCl+BaCl \rightarrow BaSO_4$$

Chemicals required: - Fusing mixture, HCl, $BaCl_2$

Apparatus: - Platinum crucible, desiccators

Procedure:-

Accurately weight 5g of sample taken in to a platinum crucible. After then it is treated with fusing mixture. Then we get a fused mass. After then it is dissolved in water and we get a sulphate. After then it is treated with HCl and $BaCl_2$ and then we get a $BaSO_4$.

$$\% \text{ Sulphur} = \frac{0.1374 \text{ X Weight of } BaSO_4}{\text{Total weight of the sample}} \text{ X } 100$$

Determination of Carbon:-

Accurately weighed 5g sample is taken into a procaine crucible (porcelain crucible). Then it is placed at heating chamber contains free weighed KOH tube and another end passing through the dry air. Then sample is heated at 110^{0}c. Then CO_2 is observes in a KOH tube. Then increase the KOH tube weight. Finally KOH tube weighed.

$$\% \text{ Carbon} = \frac{\text{Increase KOH tube Weight X } 0.2727}{\text{Total weight of the sample}} \text{ X } 100$$

Determination of Phosphorous:-

It is determined by two methods

1) Gravimetric method:-

Principle:-

It is present in the sample, it is oxidized by addition of 3 (or) 4mL of Nitric acid solution for the sample and then added to the sufficient amount of Ammonium Molybdate and then it is heated. Finally we get an Ammonium PhosphoMolybdate.

$$(NH_3)_4PO_412MoO_4+\text{Excess }NaOH\rightarrow Na_2MoO_3+Na_2HPO_4+NH_3+H_2O$$

Chemicals required: - HNO_3, Ammonium Molybdate.

Apparatus: - Platinum crucible, Desiccators.

Procedure:-

Accurately weighed 5 g of sample is taken in to a Platinum crucible. After then it is treated with HNO_3 & Ammonium Molybdate and then it is heated and then we get an Ammonium Phospho Molybdate. Finally collated in a desiccators and then it is dried and weighed as Ammonium Phospho Molybdate.

$$\%\text{ Phosphorous} = \frac{0.378 \text{ X Weight of Ammonium Phospho Molybdate}}{\text{Total weight of the sample}} \text{ X } 100$$

2) Volumetric method:-

Accurately weighed 5g of sample is taken in to a Platinum crucible. After then it is treated with HNO_3 and Ammonium Molybdate. After then it is heated and then we get Ammonium Phospho Molybdate. After then to this added excess amount of NaOH solution. The untreated NaOH is titrated with HCl by using a Phenolphthalein indicator.

$$\text{Untreated }NaOH+HCl\rightarrow NaCl+H_2O$$

Factor: - 1mL of 0.1N NaOH = 0.003088g of P_2O_5

Determination of Silica:-

Accurately weighed 5g of sample is taken in to a platinum crucible. After then it is dissolved in sufficient amount of HCl solution. After then it is treated with fusing mixture and then to produced fused mass. After then it is heated with 1:1 HCl at 500^0c for 15min. Then it is cooled in desiccators. Precipitate is formed and then filter the precipitate and then to form a residue. Here loss of weight of the sample solution.

$$\%\text{ Silica} = \frac{\text{Loss of weight of the sample}}{\text{Total weight of the sample}} \text{ X } 100$$

v) Analysis of Ferro Chromium:-

Determination of Chromium

Determination of Carbon

Determination of Silica

Determination of Chromium & FeO:-

Principle:-

Chromium exists in Ferro Chromium and then it is treated with Sodium Peroxide (Na_2O_2). We get a Na_2CrO_4 & $NaFeO_2$ mixture. Then it is dissolved in suitable solvent. We get a Fe $(OH)_3$& Na_2CrO_4 precipitate mixture, and then to this added Barium Chloride, Finally we get a Barium Chromate and Ferrous oxide.

$$FeOCr_2O_3+Na_2O_2 \rightarrow NaFeO_2+Na_2CrO_4$$

$$Na_2FeO_2+H_2O \rightarrow Fe\ (OH)_3;\ Fe\ (OH)_3 \rightarrow FeO$$

$$Na_2CrO_4+BaCl_2 \rightarrow BaCrO_4+FeO$$

Chemicals required: - Sodium Peroxide, Barium Chloride

Apparatus: - Platinum crucible, Desiccators

Procedure:-

Accurately weight sufficient amount of sample taken in to a Platinum crucible and then Chromium exists in Ferro Chromium and then it is heated with Sodium Peroxide (Na_2O_2) and then we get a $NaFeO_2$ and Na_2CrO_4. After then it is dissolved in suitable solvent like water and then we get a precipitate filter the precipitate and then residue is taken Ferric Hydroxide is present in the residue and then it is heated ,we get a Ferrous Oxide. After the filtrate is taken, Sodium Chromate present in filtrate and then to this added sufficient amount of Barium Chloride by maintain the pH 5-7.Finally we get a Barium Chromate. And then cooled sin desiccators and dried and weighed as Chromium.

$$\%\ \text{Chromium} = \frac{\text{Weight of } BaCrO_4 \text{ X } 0.2074}{\text{Total weight of the sample}} \text{ X } 100$$

$$\%\ FeO = \frac{\text{Weight of FeO X } 0.007145}{\text{Total weight of the sample}} \text{ X } 100$$

Determination of Carbon:-

Accurately weighed 5g sample is taken into a procaine crucible (porcelain crucible). Then it is placed at heating chamber contains free weighed KOH tube and another end passing through the dry air. Then sample is heated at 110^0c. Then CO_2 is observes in a KOH tube. Then increase the KOH tube weight. Finally KOH tube weighed.

$$\%\ \text{Carbon} = \frac{\text{Increase KOH tube Weight X } 0.2727}{\text{Total weight of the sample}} \text{ X } 100$$

Determination of Silica:-

Accurately weighed 5g of sample is taken in to a platinum crucible. After then it is dissolved in sufficient amount of HCl solution. After then it is treated with fusing mixture and then to produced fused mass. After then it is heated with 1:1 HCl at 500^0c for 15min. Then it is cooled in desiccators. Precipitate is formed and then filter the precipitate and then to form a residue. Here loss of weight of the sample solution.

$$\%\ \ \text{Silica} = \frac{\text{Loss of weight of the sample}}{\text{Total weight of the sample}} \text{ X } 100$$

UNIT-II

ANALYSIS OF SOIL, FERTILIZER AND FUEL

a) Analysis of Soils:-

The soil consists of so many minerals; colloidal forms etc. All these are formed in earth crush, in this so many inorganic and organic salts are presented as solid materials.

In the soil all the micro organisms are not active. All agriculture products obtained from soil. Before the analysis of soil the substance must be dried under shaded areas only, but not sunlight.

This analysis can be conducted in the laboratory (or) industries.

Sampling:-

The sampling of soils is two types.

i) Profile sampling:-

The sample get by digging the soil and it can be analyzer for the determination of particular constituents after drying it. The collection of sample is vertical cross section. It is known as profile sampling.

ii) Area sampling:-

One large area will be chosen and collect in a sample at different places by horizontal cross section is known as area sampling.

Analysis of soil can be estimated by determination of following constituents are:

Determination of Moisture

Determination of Loss of Ignition

Determination of Total Nitrogen

Determination of Phosphorous

Determination of Silica

Determination of Humus Nitrogen

Determination of Alkali salts

Determination of Lime & Soil absorption ratio

Determination of Moisture:-

The analysis can be done with almost care by heating the sample. The heating exposed continuously & the sample is mixed continuously by heating. The heating is not done for much time. After then sample is mixing & cooling & weighed. Then again repeat the procedure, until constant weight is obtained.

$$\% \text{ Moisture} = \frac{\text{Loss of weight of the sample}}{\text{Total weight of the sample}} \times 100$$

Determination of Loss of Ignition:-
The most of the sample is taken into a crucible, heat the crucible too moderately to red hot & ignite the sample at red hot. The organic matter is destroyed. Then cool the ignited sample then moisture with 2-3 drops of ammonia salts & then heated to expel ammonia gas & it is cooled & weighed. It is known as loss of ignition.

$$\% \text{ Loss of ignition} = \frac{\text{Loss of weight of the sample}}{\text{Total weight of the sample}} \text{ X } 100$$

Determination of Total Nitrogen:-

To take small amount of sample is taken into a kjeldahl flask. Then to this added HgO & concentrated H_2SO_4 & K_2SO_4. Then to increase the temperature required for the reaction & heat the solution up to destroyed for the organic matter. After then to this added antifoaming agents like $CaCl_2$ (or) Na_2CO_3 (or) paraffin's is also added. To prevents the extreme forming. Digest for 4hrs, after then the mixture is colourless and it is cooling. After then it is dilute with 200mL of water and then to this added a few pieces of granulated zinc and 25ml of K_2S solution and then solution is shaking (40g of K_2S dissolved in one liter of distilled water). The K_2S solution is added. Why because it removes all the mercury from the solution and thus prevent the formation of mercury, ammonium compounds. Then to this added 50mL of saturated solution of NaOH, then it is attached to the reflux condenser, which is placed in round bottom flask. Then the excess of NaOH is titrated with HCl by using mixed indicator (methyl red in 95%, ethanol & BromoCresol).

Factor:-18g of NH_3 = 14g of NO_2

Determination of Phosphorous:-

It is determined by two methods

1) Gravimetric method:-

Principle:-

It is present in the sample it is oxidized by addition of 3 (or) 4mL of Nitric acid solution for the sample and then added to the sufficient amount of Ammonium Molybdate and then it is heated. Finally we get an Ammonium Phospho Molybdate.

$$(NH_3)_4PO_412MoO_4\text{+Excess NaOH}\rightarrow Na_2MoO_3+Na_2HPO_4+NH_3+H_2O$$

Chemicals required: - HNO_3, Ammonium Molybdate.

Apparatus: - Platinum crucible, Desicator.

Procedure:-

Accurately weighed 5 g of sample is taken in to a Platinum crucible. After then it is treated with HNO_3 & Ammonium Molybdate and then it is heated and then we get an Ammonium Phospho Molybdate. Finally collated in a desiccators and then it is dried and then weighed as Ammonium Phospho Molybdate.

$$\% \text{ Phosphorous} = \frac{0.378 \text{ X Weight of Ammonium PhosphoMolybdate.}}{\text{Total weight of the sample}} \text{ X } 100$$

2) Volumetric method:-

Accurately weighed 5g of sample is taken in to a Platinum crucible. After then it is treated with HNO_3 &Ammonium Molybdate. After then it is heated and then we get Ammonium Phospho Molybdate. After then to this added excess amount of NaOH solution. The untreated NaOH is titrated with HCl by using a Phenolphthalein indicator.

Untreated NaOH+ HCl→NaCl+H_2O

Factor: - 1mL of 0.1N NaOH = 0.003088g of P_2O_5

Determination of Silica:-

Accurately weighed 5g of sample is taken in to a platinum crucible. After then it is dissolved in sufficient amount of HCl solution. After then it is treated with fusing mixture and then to produced fused mass. After then it is heated with 1:1 HCl at 500^0c for 15min. Then it is cooled in desiccators. Precipitate is formed and then filter the precipitate and then to form a residue. Here loss of weight of the sample solution.

$$\% \quad \text{Silica} = \frac{\text{Loss of weight of the sample}}{\text{Total weight of the sample}} \times 100$$

Determination of Humus Nitrogen:-

The amount of nitrogen present in partially decomposed organic matter is called humus nitrogen.

i) Alkaline $KMnO_4$ method:-

To take 2g of solid sample and then to this added 5mL of water and 10mL of $KMnO_4$ and 10mL of NaOH and then to attach to the condenser with reflux ,containing 0.1N H_2SO_4 & it is heated. Then the increase the temperature to boiling conditions & then reaction takes place the primary amines are converted into ammonia & then continuous the distillation up to no more ammonia fumes are obtained. Then the untreated H_2SO_4 is titrated with standard NaOH solution by using methyl red as indicator. The end point is red pink to yellow colour.

$$2KMnO_4+NaOH \rightarrow K_2O+2MnO_2+3(O)$$

$$\text{Organic matter}+3(O) \rightarrow R\text{-}NH_2$$

$$R\text{-}NH_2+H_2O \rightarrow NH_3+R\text{-}OH$$

$$NH_3+\text{Excess } H_2SO_4 \rightarrow (NH_4)_2SO_4$$

$$\text{Untreated } H_2SO_4 \rightarrow \text{Standard NaOH}$$

Factor: - 1mL of H_2SO_4 = 0.014g of Nitrogen

Available Nitrogen in PPM = $\frac{(Y-X) \times 0.014 \times N \times 10^6}{\text{Total weight of the sample}}$

Here,

Y = Volume of H_2SO_4 consumed by blank titration

X = Volume of H_2SO_4 consumed by sample titration

N = Nitrogen

ii) Determination of organic carbon method:-

In organic carbon method, the bond length present between carbon & nitrogen present in organic & inorganic is not same. That is all the nitrogen, carbon are not break at certain temperature, so this method is not recommended in the nitrogen.

Determination of Alkali salts:-

To take 0.1g of sample, which is completely dry & it is taken into a platinum crucible & then to this added few ml of water & 5mL of HF & 0.5mL of per chloride & few ml of HCl. Then HCl is decomposes the $CaCO_3$ & HF decomposes the silicates & per chloride is used to destroy the organic matter & applying the certain temperature & this procedure can be repeated 3 (or) 4 times. Then it is treated with platinum chloride. Finally we get a potassium platinum chloride precipitate. After then it is heated up to certain conditions. After then it is cooled in a desiccators, finally weighed as a potassium platinum chloride.

% KCl = 3/2 X 0.30712 X Weight of K_2PtCl_6

% NaCl = Total Alkali - % KCl

Determination of Lime & Soil absorption ratio:-

It is determined by two methods:

1) Gravimetric method:-

Principle: -

Calcium present in the sample, then calcium oxalate precipitate is formed by adding the di ammonium oxalate to the filtrate solution. Then it is heated at 500^0c, we get a calcium carbonate, again heated at 800^0-1000^0c. Then we get a CaO.

$$\text{Filtrate} + (NH_4)_2C_2O_4 \rightarrow CaC_2O_4$$

$$CaC_2O_4 \rightarrow CaCO_3$$

$$CaCO_3 \rightarrow CaO$$

Chemicals required: - Di Ammonium Oxalate

Apparatus: - Platinum crucible, Desiccators

Procedure:-

Filtrate is obtained and after then removal of Al, Fe, Cr. From the above filtrate 10mL of filtrate solution is taken into a glass beaker. After then it is treated with $(NH_4)_2C_2O_4$ and then we get a CaC_2O_4 precipitate. After then it is filter the precipitate. Filtrate is used for another analysis. After then residue is taken and then it is heated at 500^0c and then we get a $CaCO_3$. After then again heated at 800^0-1000^0c and then we get a CaO.

$$\% \text{ Calcium (or) Lime} = \frac{0.56 \text{ X Weight of CaO}}{\text{Total weight of the sample X 100}}$$

2) Volumetric method:-

Filtrate is obtained after then removal of Al, Fe; Cr. From the above filtrate solution is taken in to a glass beaker. After then to this added sufficient amount Di Ammonium Oxalate and then we get a CaC_2O_4 precipitate. After then it is dissolved in H_2SO_4 solution and then to form a $CaSO_4$ and Oxalic acid after then it is titrated with $KMnO_4$ solution.

Factor: - 1mL of 0.1N $KMnO_4$ = 0.0028g of CaO

b) Analysis of fertilizers:-

The word fertilizer indicates the fertility of crops & as well as soils can be done by using such chemicals are known as fertilizer. Fertilizers are mainly used to increase the product of crops & strength of crops. These are 3 types of fertilizers.

i) Ammonical fertilizer

ii) Phosphate fertilizer

iii) Nitrate fertilizer

i) Ammonical fertilizer:-

The following constituents are:

Determination of Moisture

Determination of Total Nitrogen

Determination of Ammonical Nitrogen

Determination of Nitrate Nitrogen

Determination of Moisture:-

The analysis can be done with almost care by heating the sample. The heating exposed continuously & the sample is mixed continuously by heating. The heating is not done for much time. After then sample is mixing & cooling & weighed. Then again repeat the procedure, until constant weight is obtained.

$$\% \text{ Moisture} = \frac{\text{Loss of weight of the sample}}{\text{Total weight of the sample}} \times 100$$

Determination of Total Nitrogen:-

To take small amount of sample is taken into a kjeldahl flask. Then to this added HgO & concentrated H_2SO_4 & K_2SO_4. Then to increase the temperature required for the reaction & heat the solution up to destroyed for the organic matter. After then to this added antifoaming agents like $CaCl_2$ (or) Na_2CO_3 (or) paraffin's is also added. To prevents the extreme forming. Digest for 4hrs, after then the mixture is colourless and it is cooling. After then it is dilute with 200mL of water and then to this added a few pieces of granulated zinc and 25ml of K_2S solution and then solution is shaking (40g of K_2S dissolved in one liter of distilled water). The K_2S solution is added. Why because it removes all the mercury from the solution and thus prevent the formation of mercury, ammonium compounds. Then to this added 50mL of saturated solution of NaOH, then it is attached to the reflux condenser, which is placed in round bottom flask. Then the excess of NaOH is titrated with HCl by using mixed indicator (methyl red in 95%, ethanol & Bromo Cresol).

$$\% \text{ Nitrogen} = \frac{\text{Volume of Acid X Normality of Acid X } 0.014008}{\text{Total weight of the sample}} \times 100$$

$$\% \text{ Ammonia} = \frac{\text{Volume of Acid X Normality of Acid X } 0.01703}{\text{Total weight of the sample}} \times 100$$

Determination of Ammonical Nitrogen:-

Accurately weighed 0.7-3.5g of fertilizer sample is taken into a distillation flask. Then to this added 200mL of water & 5g of MgO is added. It is used to free from carbonates. Then it is connect to the flask with a condenser. After then ammonia gas is evolved, then it is passes through receiver flask contains excess amount of H_2SO_4. Then the untreated H_2SO_4 is titrated with NaOH by using suitable indicator.

$$\% \text{ Ammonical Nitrogen} = \frac{\text{Volume of Acid X Normality of Acid X 0.014008}}{\text{Total weight of the sample}} \text{ X 100}$$

Determination of Nitrate Nitrogen:-

Dissolve 10g of sample in 500mL of water, from the above solution 25mL of solution is taken into a distillation flask. Then to this added 120mL of distilled water & 5g of zinc & 5g of reduced iron is added. Connect the flask with a condenser. After then ammonia gas is evolved & then it is passes through a receiver flask & also contain excess amount of H_2SO_4. Then the untreated H_2SO_4 is titrated with standard NaOH buy using suitable indicator. The nitrogen obtained represents the nitrate nitrogen + ammonical nitrogen, so we can subtract the ammonical nitrogen from total nitrate nitrogen + ammonical nitrogen. Finally we get nitrate nitrogen.

% Nitrate Nitrogen = [Nitrate Nitrogen + Ammonical Nitrogen]-Ammonical Nitrogen

ii) Phosphate fertilizer:-

The following constituents are:

Determination of Total Phosphorous

Determination of Water Soluble Phosphorous

Determination of Citrate Soluble Phosphorous

Determination of Calcium

Determination of Sodium

Determination of Potassium

Determination of Total Phosphorous:-

It is determined by two methods

1) Gravimetric method:-

Principle:-

It is present in the sample it is oxidized by addition of 3 (or) 4mL of Nitric acid solution for the sample and then added to the sufficient amount of Ammonium Molybdate and then it is heated. Finally we get an Ammonium Phospho Molybdate.

$$(NH_3)_4PO_412MoO_4\text{+Excess NaOH}\rightarrow Na_2MoO_3+Na_2HPO_4+NH_3+H_2O$$

Chemicals required: - HNO_3, Ammonium Molybdate.

Apparatus: - Platinum crucible, Desicator.

Procedure:-

Accurately weighed 5 g of sample is taken in to a Platinum crucible. After then it is treated with HNO_3 & Ammonium Molybdate and then it is heated and then we get an Ammonium Phospho Molybdate. Finally collated in a desiccators and then it is dried and then weighed as Ammonium Phospho Molybdate.

$$\% \text{ Phosphorous} = \frac{0.378 \times \text{Weight of Ammonium PhosphoMolybdate.}}{\text{Total weight of the sample}} \times 100$$

2) Volumetric method:-

Accurately weighed 5g of sample is taken in to a Platinum crucible. After then it is treated with HNO_3 & Ammonium Molybdate. After then it is heated and then we get Ammonium Phospho Molybdate. After then to this added excess amount of NaOH solution. The untreated NaOH is titrated with HCl by using a Phenolphthalein indicator.

$$\text{Untreated NaOH} + HCl \rightarrow NaCl + H_2O$$

Factor: - 1mL of 0.1N NaOH = 0.003088g of P_2O_5

Determination of Water Soluble Phosphorous:-

Accurately weighed 1g of sample is taken into what man filter paper. After then it is placed in a funnel. The funnel can be kept in to a conical flask. After then the sample can be washed with distilled water. Then turbidity (or) precipitate is obtained. After then to this added 2 (or) 3 ml of HNO_3 solution. After then it is treated with excess amount of NaOH. Finally the untreated NaOH is titrated with HCl by using methyl orange as an indicator.

Determination of Citrate Soluble Phosphorous:-

Accurately weighed 1g of sample is taken in to a beaker, and then to this added 2-3 ml of HNO_3. After then to this added ammonium molybdate solution. We get Ammonium Phospho Molybdate. This weight is represented as total phosphorous.

Accurately weighed 1g of sample is taken in to a beaker, then to this added sufficient amount of ammonium citrate solution. The substance can be not dissolved in ammonium citrate solution, then to this added 5ml of CH_3COOH & 2-3ml of HNO_3 & few ml of 1:1 HCl. After then it is dissolved. After then to this added ammonium molybdate. Finally we get Ammonium Phospho Molybdate precipitate. After then it is dried & weighed. This weight can be represented as citrate soluble phosphorous. Finally citrate soluble phosphorous can be subtracted from the total phosphorous. Finally we get a citrate soluble phosphorous.

Determination of Lime (Calcium):-

It is determined by two methods:

1) Gravimetric method:-

Principle: -

Calcium present in the sample, then calcium oxalate precipitate is formed by adding the di ammonium oxalate to the filtrate solution. Then it is heated at 500^0c, we get a calcium carbonate, again heated at 800^0-1000^0c. Then we get a CaO.

$$\text{Filtrate} + (NH_4)_2C_2O_4 \rightarrow CaC_2O_4$$

$$CaC_2O_4 \rightarrow CaCO_3$$

$$CaCO_3 \rightarrow CaO$$

Chemicals required: - Di Ammonium Oxalate

Apparatus: - Platinum crucible, Desiccators

Procedure:-

Filtrate is obtained and after then removal of Al, Fe, Cr. From the above filtrate 10mL of filtrate solution is taken into a glass beaker. After then it is treated with $(NH_4)_2C_2O_4$ and then we get a CaC_2O_4 precipitate. After then it is filter the precipitate. Filtrate is used for another analysis. After then residue is taken and then it is heated at 500^0c and then we get a $CaCO_3$. After then again heated at 800^0-1000^0c and then we get a CaO.

$$\% \text{ Calcium (or) Lime} = \frac{0.56 \times \text{Weight of CaO}}{\text{Total weight of the sample} \times 100}$$

2) Volumetric method:-

Filtrate is obtained after then removal of Al, Fe; Cr. From the above filtrate solution is taken in to a glass beaker. After then to this added sufficient amount Di Ammonium Oxalate and then we get a CaC_2O_4 precipitate. After then it is dissolved in H_2SO_4 solution and then to form a $CaSO_4$ and Oxalic acid after then it is titrated with $KMnO_4$ solution.

Factor: - 1mL of 0.1N $KMnO_4$ = 0.0028g of CaO

Determination of Alkali salts:-

To take 0.1g of sample, which is completely dry & it is taken into a platinum crucible & then to this added few ml of water & 5mL of HF & 0.5mL of per chloride & few ml of HCl. Then HCl is decomposes the $CaCO_3$ & HF decomposes the silicates & per chloride is used to destroy the organic matter & applying the certain temperature & this procedure can be repeated 3 (or) 4 times. Then it is treated with platinum chloride. Finally we get a potassium platinum chloride precipitate. After then it is heated up to certain conditions. After then it is cooled in a desiccators, finally weighed as a potassium platinum chloride.

% KCl = 3/2 X 0.30712 X Weight of K_2PtCl_6

% NaCl = Total Alkali - % KCl

iii) Nitrate fertilizer:-

Thse following constituents are:

Determination of Moisture

Determination of Total Nitrogen

Determination of Ammonical Nitrogen

Determination of Nitrate Nitrogen

Determination of Moisture:-

The analysis can be done with almost care by heating the sample. The heating exposed continuously & the sample is mixed continuously by heating. The heating is not done for much time. After then sample is mixing & cooling & weighed. Then again repeat the procedure, until constant weight is obtained.

$$\% \text{ Moisture} = \frac{\text{Loss of weight of the sample}}{\text{Total weight of the sample}} \text{ X } 100$$

Determination of Total Nitrogen:-

To take small amount of sample is taken into a kjeldahl flask. Then to this added HgO & concentrated H_2SO_4 & K_2SO_4. Then to increase the temperature required for the reaction & heat the solution up to destroyed for the organic matter. After then to this added antifoaming agents like $CaCl_2$ (or) Na_2CO_3 (or) paraffin's is also added. To prevents the extreme forming. Digest for 4hrs, after then the mixture is colourless and it is cooling. After then it is dilute with 200mL of water and then to this added a few pieces of granulated zinc and 25ml of K_2S solution and then solution is shaking (40g of K_2S dissolved in one liter of distilled water). The K_2S solution is added. Why because it removes all the mercury from the solution and thus prevent the formation of mercury, ammonium compounds. Then to this added 50mL of saturated solution of NaOH, then it is attached to the reflux condenser, which is placed in round bottom flask. Then the excess of NaOH is titrated with HCl by using mixed indicator (methyl red in 95%, ethanol & Bromo Cresol).

$$\% \text{ Nitrogen} = \frac{\text{Volume of Acid X Normality of Acid X } 0.014008}{\text{Total weight of the sample}} \text{ X } 100$$

$$\% \text{ Ammonia} = \frac{\text{Volume of Acid X Normality of Acid X } 0.01703}{\text{Total weight of the sample}} \text{ X } 100$$

Determination of Ammonical Nitrogen:-

Accurately weighed 0.7-3.5g of fertilizer sample is taken into a distillation flask. Then to this added 200mL of water & 5g of MgO is added. It is used to free from carbonates. Then it is connect to the flask with a condenser. After then ammonia gas is evolved, then it is passes through receiver flask contains excess amount of H_2SO_4. Then the untreated H_2SO_4 is titrated with NaOH by using suitable indicator.

$$\% \text{ Ammonical Nitrogen} = \frac{\text{Volume of Acid X Normality of Acid X } 0.014008}{\text{Total weight of the sample}} \text{ X } 100$$

Determination of Nitrate Nitrogen:-

Dissolve 10g of sample in 500mL of water, from the above solution 25mL of solution is taken into a distillation flask. Then to this added 120mL of distilled water & 5g of zinc & 5g of reduced iron is added. Connect the flask with a condenser. After then ammonia gas is evolved & then it is passes through a receiver flask & also contain excess amount of H_2SO_4. Then the untreated H_2SO_4 is titrated with standard NaOH buy using suitable indicator. The nitrogen obtained represents the nitrate nitrogen + ammonical nitrogen, so we can subtract the ammonical nitrogen from total nitrate nitrogen + ammonical nitrogen. Finally we get nitrate nitrogen.

% Nitrate Nitrogen = [Nitrate Nitrogen + Ammonical Nitrogen]-Ammonical Nitrogen

c) Analysis of fuels:-

Fuels play an important role in daily life of mankind. Fuels are in dispersible in presented world. The fuels are used to produce heat energy. These are used in many ways for domestic & industrial purposes.

Fuel is defined as combustible substance & containing carbon as main constituents which on proper burning which gives a large amount of heat.

$$CnH_{2n+2} + (3n+1/2)\ O_2 \rightarrow nCO_2 + (n+1)\ H_2O + \text{heat}$$

Classification of fuels:-

Fuels are classified based on Occurrence & Physical state.

Classification of based on Occurrence:-

Fuels are two types based on Occurrence, there are

i) Natural (or) Primary fuels

ii) Artificial (or) Secondary fuels

i) Natural (or) Primary fuels:-

These are fuels which occur in nature is called as Primary fuels (or) Natural fuels.

Ex: - Wood, Coal, Natural gas

ii) Artificial (or) Secondary fuels:-

These are fuels which are prepared from primary fuels is called Secondary fuels (or) Artificial fuels.

Ex: - Charcoal, Petrol, Kerosene, Diesel...

Classification of based on Physical state:-

Fuels are three types based on Physical state, there are

i) Solid fuels

ii) Liquid fuels

iii) Gases fuels

i) Solid fuels:-

The fuel present in solid state is known as solid state fuels.

Ex: - Coke, Coal, Wood

ii) Liquid fuels:-

The fuel present in liquid state is known as liquid state fuels.

Ex:-Petrol, kerosene, Diesel

iii) Gases fuels:-

The fuel present in gases state is known as gases state fuels.

Ex:-Water gas ($CO+H_2$), Produced gas ($CO+H_2+N_2$), Natural gas (Methane gas), and Coal gas.

In metallurgical industrials only coke, coal are of importance as fuels. Hence the coke & coal is discussed here various tests & analysis applied to coal in order to assess their properties may be grouped under 3 catagerious. There is solid fuels-coal analysis.

1) Proximate analysis

2) Ultimate analysis

3) Addition tests

1) Proximate analysis of coal:-

The following constituents are:

Determination of Moisture

Determination of Ash

Determination of Volatile matter

Determination of Fixed Carbon

Determination of Sulphur

Determination of Moisture:-

Accurately weighed 1g of coal sample is taken into a platinum crucible & then it is heated & cooled in desiccators over concentrated H_2SO_4.Now crucible placed in a special moisture oven & dry for exactly one hour at 104-108^{0}C.After heating it is cooled in desiccators & dry it. Finally loss of the weight is obtained from this we can calculate the weight of the moisture.

$$\% \text{ Moisture} = \frac{\text{Loss of weight of the sample}}{\text{Total weight of the sample}} \times 100$$

Determination of Ash:-

Place the crucible containing the dried coal from the moisture determination in a muffle furnace. Now heat the crucible at 400^{0}C, until most of the organic matter is burner off & heating for one hour at 750^{0}C to complete the combustion, cooled in desiccators & then finally weighed.

$$\% \text{ Ash} = \frac{\text{Weight of the sample}}{\text{Total weight of the sample}} \times 100$$

Determination of Volatile matter:-

Accurately weighed 1g of sample is taken into a platinum crucible & placed on a Nichrome wire triangle & heat for exactly 7min. hence the temperature must be maintain at 950^{0}C. After heating exactly 7min, remove the crucible & it is cooled.

$$\% \text{ Moisture} = \frac{\text{Loss of weight} - \text{Weight of the sample}}{\text{Total weight of the sample}} \times 100$$

Determination of Fixed Carbon:-

The sum of the total of the percentage of volatile matter, moisture & ash subtracted from the 100 gives the percentage of fixed carbon.

% fixed carbon = 100-(% moisture +Ash +Volatile matter)

Determination of Sulphur:-

Accurately weighed 1.3g of coal sample is taken into a procaine (procaline) crucible. After then to this added 3g of eschka mixture (2 parts of MgO + 1 part of anhydrous Na_2CO_3) & it is covered with 1g of eschka mixture. After then it is placed in to a muffle furnace & gradually rise to temperature at 870-950^{0}C for one hour. After heating it is transferred into a beaker & digests with 100ml of hot water with occasional stirring, then it is filter, filtrate is taken and then to this added 5ml of bromine water & 2ml of concentrated HCl. It is boiled to expel the liberated bromine, now solution is neutralized with Na_2CO_3 (or) 2ml of HCl. Finally then to this added 10% of 10ml of $BaCl_2$ solution, then we get a $BaSO_4$ precipitate. It is filter by using ash less filter paper & wash with hot water. It is taken into a platinum crucible and it is heated to approximately 900^{0}C, until constant weight is obtained. Then it is cooled in desiccators & weighed as $BaSO_4$ precipitate.

% Sulphur = Weight of $BaSO_4$ X 10

2) Ultimate analysis:-

The following constituents are:

Determination of Moisture

Determination of Ash

Determination of Carbon & Hydrogen

Determination of Oxygen

Determination of Sulphur

Determination of Nitrogen

Determination of Moisture:-

Accurately weighed 1g of coal sample is taken into a platinum crucible & then it is heated & cooled in desiccators over concentrated H_2SO_4.Now crucible placed in a special moisture oven & dry for exactly one hour at 104-108^{0}C.After heating it is cooled in desiccators & dry it. Finally loss of the weight is obtained from this we can calculate the weight of the moisture.

$$\% \text{ Moisture} = \frac{\text{Loss of weight of the sample}}{\text{Total weight of the sample}} \text{ X } 100$$

Determination of Ash:-

Place the crucible containing the dried coal from the moisture determination in a muffle furnace. Now heat the crucible at 400^{0}C, until most of the organic matter is burner off & heating for one hour at 750^{0}C to complete the combustion, cooled in desiccators & then finally weighed.

$$\% \text{ Ash} = \frac{\text{Weight of the sample}}{\text{Total weight of the sample}} \text{ X } 100$$

Determination of Carbon & Hydrogen:-

Accurately weighed 0.2g of coal sample is taken in to a Procaine crucible. Then it is placed in a heating chamber consists of two ends. One end is connected to free weighed KOH tube & another end is connected to free weighed $CaCl_2$ tube. Now the sample is heated, during the heating, the carbon is present in the sample. Then it is converted in to CO_2 & it is observed by the KOH tube. The hydrogen is present in the sample. Then it is converted into H_2O & it is observed by the $CaCl_2$ tube. After then heating applied continuously, until tubes obtained constant weight. The difference in weight of tubes gives the amount of carbon & hydrogen present in the sample.

$$\% \text{ Hydrogen} = \frac{\text{Increasing the } CaCl_2 \text{ tube weight} \times 11.9}{\text{Total weight of the sample}} \times 100$$

$$\% \text{ Carbon} = \frac{\text{Increasing the KOH tube weight} \times 0.2728}{\text{Total weight of the sample}} \times 100$$

Determination of Oxygen:-

Oxygen can be determined there is no exact method. So it can be subtracted by total percentages of moisture, ash, carbon, hydrogen, nitrogen, sulphur from 100 gives the weight of the oxygen.

% Oxygen = 100- (% Moisture + Ash + carbon +Hydrogen + Nitrogen + Sulphur)

Oxygen weight cannot be exact determination.

Determination of Sulphur:-

Accurately weighed 1.3g of coal sample is taken into a procaine (procaline) crucible. After then to this added 3g of eschka mixture (2 parts of MgO+1 part of anhydrous Na_2CO_3) & it is covered with 1g of eschka mixture. After then it is placed in to a muffle furnace & gradually rise to temperature at 870-950^{0}C for one hour. After heating it is transferred into a beaker & digests with 100ml of hot water with occasional stirring, then it is filter, filtrate is taken and then to this added 5ml of bromine water & 2ml of concentrated HCl. It is boiled to expel the liberated bromine, now solution is neutralized with Na_2CO_3 (or) 2ml of HCl. Finally then to this added 10% of 10ml of $BaCl_2$ solution, then we get a $BaSO_4$ precipitate. It is filter by using ash less filter paper & wash with hot water. It is taken into a platinum crucible and it is heated to approximately 900^{0}C, until constant weight is obtained. Then it is cooled in desiccators & weighed as $BaSO_4$ precipitate.

% Sulphur = Weight of $BaSO_4$ X 10

Determination of Nitrogen:-

To take small amount of sample is taken into a kjeldahl flask. Then to this added HgO & concentrated H_2SO_4 & K_2SO_4. Then to increase the temperature required for the reaction & heat the solution up to destroyed for the organic matter. After then to this added antifoaming agents like $CaCl_2$ (or) Na_2CO_3 (or) paraffin's is also added. To prevents the extreme forming. Digest for 4hrs, after then the mixture is colourless and it is cooling. After then it is dilute with 200mL of water and then to this added a few pieces of granulated zinc and 25ml of K_2S solution and then solution is shaking (40g of K_2S dissolved in one liter of distilled water). The K_2S solution is added. Why because it removes all the mercury from the solution and thus prevent the formation of mercury, ammonium compounds. Then to this added 50mL of saturated solution of NaOH, then it is attached to the reflux condenser, which is placed in round bottom flask. Then the excess of NaOH is titrated with HCl by using mixed indicator (methyl red in 95%, ethanol & BromoCresol).

Factor:-18g of NH_3 = 14g of NO_2

Heating value (or) calorific value:-

The quality of the fuel is determined by its calorific value. Calorific value of the fuel is the total quantity of heat liberated when a unit mass of the fuel is burn completely. It s called as Heating value (or) Calorific value.

Units of calorific value:-

Calorific value is generally expressed in cal/gm or k.cal/k.gm (or) British thermal units/pound. Gaseous fuels can be represented as k.cal/m^3.

Classification of calorific value:-

It is classified into 2 types.

i) Higher calorific value (HCV)

ii) Lower calorific value (LCV)

i) Higher calorific value (HCV):-

When fuels are undergoing combustion, hydrogen present in the fuel is converted in to stream. The products of combustion are condensed to room temperature the condensation of the stream also liberated (is equal) same energy. The total heat liberated is equal to some of heat liberated on combustion of the heat & the energy liberated due to liquefaction of water. This heat liberated is known as ‘Higher calorific value’.

(OR)

Higher calorific value is the total amount of heat produced by when a unit mass of the fuel as been burn completely and the products of combustion have been cool done to room temperature higher calorific value is also known as ‘Gross calorific value’.

ii) Lower calorific value (LCV):-

If the calorific value of the fuel is determined without allowing the products to cool done the calorific value is known as ‘Lower calorific value’.

(OR)

Lower calorific value is the net heat produced when a unit mass of fuel is burn completely & the products are permitted to escape. LCV is lesser than the HCV. LCV is also known as ‘Net calorific value’.

LCV=HCV-latent heat of vaporization.

Grading of coal based on Ultimate Heat Value (UHV):-

Here the formations of the coal slow decomposition of organic matter under at higher temperature & pressure by the limited supply of oxygen.

It consists of mixture several elements in various proportions. Grading of coal depends up on the percentage of carbon present in the coal. Coal can be divided into 4 types.

i) Peat coal

ii) Lignite coal

iii) Bituminous coal

iv) Anthracite coal

i) Peat coal:- 60% of carbon containing of coal is called peat coal. It has low stage carbon. So it has low calorific value, which is around 5450k.cal/k.gm

ii) Lignite coal:- 60-75% carbon containing coal is called lignite coal the calorific value is 5800-7000k.cal/k.g. Lignite coal occurs in Madhya Pradesh, Assam, Kashmir, Rajas tan & Tamilanad.

iii) Bituminous coal:- 75-82% carbon containing coal is called bituminous coal. The calorific value is 7000 k.cal/k.g. it is very commonly used for domestic purpose. This is occurred in Bihar, Madhya Pradesh, and Bengal & Orissa.

iv) Anthracite coal:- It can be consider as highest rank of the coal. It contains 92-96% carbon. It contains calorific value is 8600k.cal/k.g. It is found in Jammu, Dazzling.

Additional input:-

Determination of calorific value by using Bomb calorimeter in coal analysis :-(Diagram)

This is commonly used to find the heat of combustion of organic substances. It consists of a sealed combustion chamber is called a bomb. A weighed quantity of substance is taken into a dish along with oxygen under about 20atm.pressure is placed in the 'Bomb'. The lowered in water contained in an insulated copper vessel. The vessel is fitted with a stirrer & sensitive thermometer the arrangement is shown in figure. The temperature of water is noted & the substance is ignited by an electric current. After combustion the rise in temperature of system is noted. The heat of combustion is calculated from the heat gain by calorimeter.

$$\text{Calorific value} = \frac{t\,(W + w)}{X}$$

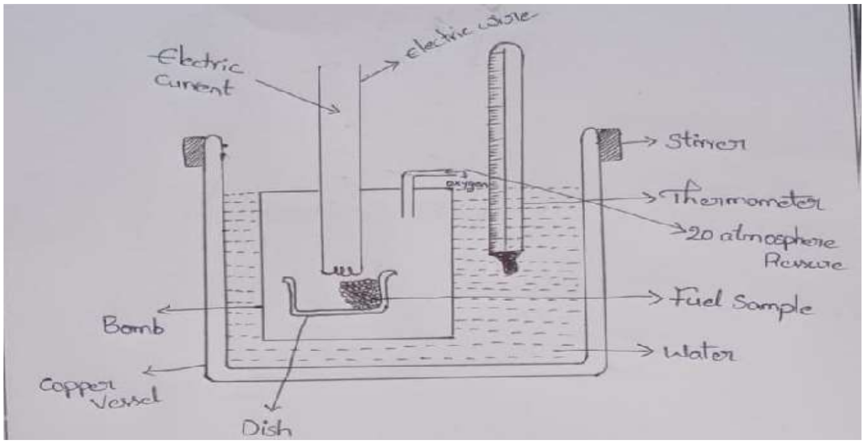
Here,

t = Temperature

w = Quantity of coal added

W = Weight of water

x = Weight of the sample



UNIT-III

ASSESSMENT OF AIR QUALITY

Assessment of air quality:-

Air quality is measured with the Air Quality Index. The AQI works like a thermometer that runs from 0 to 500 degrees. However, instead of showing changes in the temperature, the AQI is a way of showing changes in the amount of pollution in the air.

Air quality:-

An air quality index is used by government agencies to communicate to the public how polluted the air currently is or how polluted it is forecast to become. Public health risks increase as the AQI rises. Different countries have their own air quality indices, corresponding to different national air quality standards.

Composition of pure air:-

There is no chemical formula for air as it is a mixture of many compounds. The major components would be Nitrogen (N_2), Oxygen (O_2), Carbon Dioxide (CO_2), Water (H_2O), and many others in minute amounts. Nitrogen makes up 78.1% of air, while oxygen makes up 20.9% of air. The components of atmosphere is classified into three groups as major, minor & trace components from pollution free dry air at ground level in components as expressed percentage of volume as follows.

Components	concentration in		Estimated residence time
	Average conc. (PPM)	Volume percent	
Major components:-			
Nitrogen (N_2)	$78.09X10^4$	78.09	continuous
Oxygen (O_2)	$20.94X10^4$	20.1	continuous
Water vapor	-	0.1-5	continuous
Minor components:-			
Argon (Ar)	$9.3X10^2$	0.93	continuous
Carbon dioxide (CO_2)	$32X10^2$	0.0318	2-4 years
Trace components:-			
Neon (Ne)	18	0.0018	continuous
Hydrogen (H_2)	0.5	0.000005	Little time
Helium (He)	5.2	0.00052	~2 million years
Krypton (Kr)	1.0	0.0001	continuous
Xenon (Xe)	0.081	-	continuous
Ozone (O_3)	0.02	0.000002	~60 days
Ammonia (NH_3)	0.01	0.000001	~7 days
Methane (CH_3)	1.3	0.00013	4-7 years
Carbon monoxide (MO)	0.1	0.00001	0-5 years
Nitrogen dioxide (NO_2)	0.001	0.0000001	05 days
Sulphur dioxide (SO_2)	0.0002	0.0000001	04 days
Hydrogen sulphide (HS)	0.002	0.00002	02 days

Air pollution:-

It is a mixture of solid particles and gases in the air. Car emissions, chemicals from factories, dust, and pollen and mold spores may be suspended as particles. Ozone, a gas, is a major part of air pollution in cities. When ozone forms air pollution, it's also called smog. Some air pollutants are poisonous. Pollution can hurt water, soil, and air. Examples of air pollutants are carbon dioxide from burning fossil fuels, and sulfur dioxide. A lack of clean air can be problematic for not only humans, but also plants, animals, and bacteria in the ecosystem.

Classification of air pollution:-

There are two types of pollutants.

1. Primary air pollutants

2. Secondary air pollutants

1. Primary pollutants:-

There are different categories are such pollutants that present in air is called primary (or) natural air pollutants. The primary pollutants are emitted directly from the identifiable sources.

E.g.:- vehicles, industries and volcanoes etc.

Primary pollutants are classified as:-

A. Oxides of carbon →Carbon monoxide (CO) & Carbon dioxide (CO_2)

B. Oxides of sulphure→SO_2, Sulphur trioxide SO_3, Hydrogen sulphide (H_2S)

C. Oxides of Nitrogen →Nitric oxide (NO), Nitrogen dioxide (NO_2)

D. Hydro carbons →Aliphatic hydrocarbons, polycyclic aromatic hydrocarbons

E. Particulate matter →Responsible & suspended particulate matter, inorganic & organic particulates.

2. Secondary pollutants:-

Primary pollutants are reacting themselves (or) it may react with water vapor & it format entirely new product in the presence of sunlight such product is called secondary pollutants.

A. Peroxy acetyl nitrate (PAN)

B. Peroxy benzyl nitrate (PBN)

C. Ozone (O_3)

Primary pollutants are emitted from natural sources directly into the atmosphere, while secondary pollutants result from the chemical reactions or the physical interactions between the primary pollutants themselves or between the primary pollutants and other atmospheric components.

Toxic elements present in dust & their sources:-

Heavy metals such as arsenium, lead and mercury can result in serious health risks (e.g. Lung damage, kidney diseases, nervous system failures) & can be harmful to the environment (**e.g.** Soil & water pollution, plants).

1. Lead (Pb^{+2}):-

Sources:-

The major sources are lead in atmosphere is,

1. Combustion of leaded petrol

2. Combustion of gasoline (petrol + ethanol)

Here the hydro carbons are 50-80% in motor fuel.

They are two types of leaded petrol available they are,

$Pb(CH_3)_4$ →Tetra methyl lead

$Pb(C_2H_5)_4$ → Tetra ethyl lead & these are measured at the absorbance level $2833A^O$

Natural sources:-

Natural sources are producing considerable pollutants but in the evolution most of these things are essential components of a balanced ecosystem. These sources are a raised from the naturally.

Here forest fires (69%), volcanic eruption (or) action.

Sulphur springs Marsh gases.

Man made sources:-

These are sources a raised from the man activities.

E.g.:-Motor vehicles (59.5%), Automobiles, Burning of coals, burning of fuels. Deforestation, mining, metallurgy, agricultural activities, waste treatment plant.

Power generation, industrial process (iron, steel, paper, & petroleum industries),

Mainly these are manmade sources.

The Automobiles are sources of lead particles in the atmosphere. Combustion of leaded gasoline discharged lead halides though the exhaust system.

$$Pb(C_2H_5)_4 + O_2 \text{ (halogenated scavengers)} \rightarrow PbCl_2+PbBr_2)$$

(A halogenated scavenger means dichloride ethane or dibromo ethane + CO_2 + H_2O +PbBrCl).

In recent years however this quality is decreasing with the use of unleaded gasoline.

Effects:-

Effects of organic lead:-

Most effect of tetra ethyl lead & tri methyl lead upon the nervous system. They first show as sleepless & irritation.

If the high percentage of lead liberate in atmosphere they cause effect on hallucinations, vision & hearing.

At low persistent levels they cause headache, general fatigue & sometimes depression.

Effects of inorganic acid:-

1. Inorganic lead is poising also starts with fatigue & irritability but it is often accompanied by Anemia & abdominal pain.

2. The anemia is mainly due to fact that one of the early enzymes of haemoid synthesis, D- aminolevulinic acid dehydrates inhibited by inorganic lead while RBCs shows increased fragility & have shortened life spans.

It's also known as an erythrocyte count. The test is important because RBCs contain hemoglobin, which carries oxygen to your body's tissues. The number of RBCs you have can affect how much oxygen your tissues receive. Your tissues need oxygen to function.

3. Inorganic lead may increase blood pressure and in children disturb the metabolism of vitamin 'D' which effects the growth of their long bones.

4. Inorganic lead also affects kidneys. Generally slowing of nerve is impulses occur with both inorganic & organic forms of lead. Lead is present in the body can be remove as the follows. This is removing in the form of urine.

$$PO_4^{-3} + Pb \rightarrow Pb_3\ (PO_4^{-2})$$

$$\text{Ca-Chelate} + Pb \rightarrow Pb\ \text{–Chelate} + Ca^{+2}$$

Effects of human beings:-

1. The exposure to high levels of lead may cause anemia, weakness & kidney, brain damage. Very high exposure can cause death. Lead can damage a developing baby's nervous system.

2. Young children are particularly vulnerable to the toxic effects of lead & can suffer profound and permanent adverse health effects.

3. Particularly affecting the developing of the brain & nervous system. Lead also causes long – term harm in adults, including increased risk of high blood pressure & kidney damage.

4. Lead is a toxic metal & very strong poison. Heavy metals are toxic to human beings. Even small amounts of lead can cause serious health problems.

5. Lead serves no useful purpose in the human being. Lead effects on human beings are hormonal status, enzyme, activity, membrane structure, water potential in our body's.

2. Mercury [Hg (II)]:-

Sources:-

The major sources are ‘Hg’ in chloro alkali industries. In which alkali & Cl_2 are produced by electrolysis. Intermediate sources are electrical industries in which H_2S is used. This source is agriculture industries in which pesticides containing mercury (Hg (II)).

Natural abundance of mercury is in the level of 0.1 ppb & the sources are volcanoes, due to volcanoes explosion 8.0 ppb Hg released into atmosphere. Major sources are cinnabar [HgS] & due to fossil fuel < 1, coals exhibit 100 ppb. Due to ‘Hg’ we observe psychopathological symptoms like dryness.

Natural sources:-

Natural sources are producing considerable pollutants but in the evolution most of these things are essential components of a balanced ecosystem.

These sources are a raised from the naturally.

Forest fires (69%), volcanic eruption (or) action, Sulphur springs Marsh gases.

Man made sources:-

These are sources a raised from the man activities.

E.g.:-Motor vehicles (59.5%), Automobiles, burning of coals, burning of fuels. Deforestation, mining, metallurgy, agricultural activities, waste treatment plant, power generation, industrial process (iron, steel, paper, & petroleum industries),

Mainly these are manmade sources.

Effects:-

Minamata disease:-

Minamata disease was first discovered in the city of Minamata in Japan in 1956. It was caused by the release of methyl mercury in the industrial wastewater from a chemical factory owned by the Chisso Corporation, which continued from 1932 to 1968. The cause of Minamata disease is the methyl mercury contaminated wastewater released from a factory in the area. Minamata disease can be contracted by eating seafood polluted by methyl mercury.

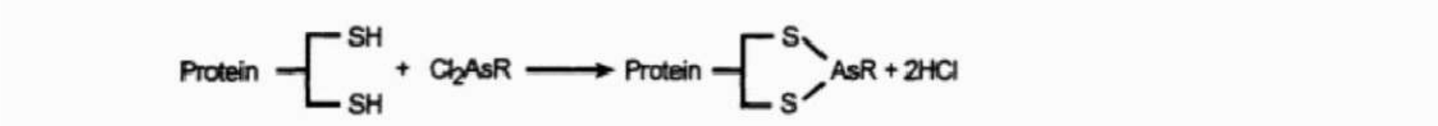
This is a disorder caused by methyl mercury poisoning that was first described in the inhabitants of Minamata Bay, Japan & resulted from their eating fish contaminated with mercury industrial waste.

Minamata disease, sometimes referred to as Chisso-Minamata disease, is a neurological disease caused by severe mercury poisoning, numbness in the hands and feet, general muscle weakness, damage to hearing and speech, neurological symptoms. Thousands of peoples lost their life’s & thousands of peoples are genetic effects are observed in the bodies. The main treatments involve the temporary relief of symptoms (symptomatic therapy), & rehabilitation (physiotherapy & occupational therapy).

3. Arsenic [As (III)]:-

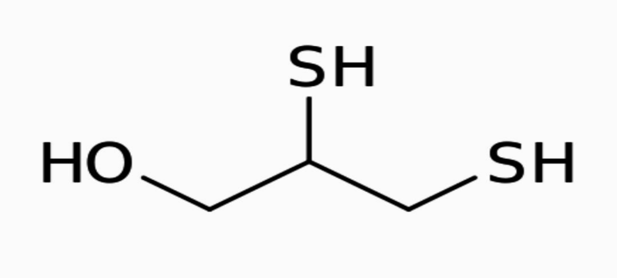
Arsenic poisoning is a medical condition that occurs due to elevated levels of arsenic in the body. If arsenic poisoning occurs over a brief period of time, symptoms may include vomiting, abdominal pain, and watery diarrhea that contain blood. Soluble inorganic arsenic can have immediate toxic effects. Ingestion of large amounts can lead to gastrointestinal symptoms such as severe vomiting, disturbances of the blood and circulation, damage to the nervous system, and eventually death.

Arsenic compound commonly occurs in insecticides, fungicides, and herbicides these among its compounds As (III) are the most toxic. As (III) exits its toxic action by attacking 'SH' groups of an enzyme there is inhibiting enzyme action.



As (III) is removed by body is treating with 2, 3-dimercaptopropanol. As (III) compounds at higher concentrations coagulate proteins possible by attacking the sulphur bonds maintaining the secondary & tertiary structures of proteins.

The structure of 2, 3- dimercaptopropanol is,



a) Primary pollutants:-

i). Carbon compounds:-

1. Carbon monoxide (CO)

2. Carbon dioxide (CO_2)

1. Determination of Carbon monoxide (CO):-

Sources:-

Natural sources:-

Natural sources are producing considerable pollutants but in the evolution most of these things are essential components of a balanced ecosystem. These sources are a raised from the naturally.

Forest fires (69%), volcanic eruption (or) action, sulphur springs (gas)**,** marsh gases.

Man made sources:-

These are sources a raised from the man activities.

E.g.:-Motor vehicles (59.5%), Automobiles, burning of coals, burning of fuels. Deforestation, mining, metallurgy, agricultural activities, waste treatment plant, power generation, industrial process (iron, steel, paper, & petroleum industries), Mainly CO is generated from the burning of coal, gasoline, motor exhaust.

Sinks of 'CO':-

The possible sinks of 'CO' are atomic oxygen, hydroxyl radicals & oxides of micro organisms, plants are sinks of 'CO'.

Reactions of 'CO':-

$$CO+O_2 \rightarrow CO_2$$

$$:OH+CO \rightarrow CO_2+H$$

Content in the atmosphere:-

Global concentration average = 0.1ppm

Local area = 0.5ppm

Effects:-

1. Effects of 'CO' on human beings.

2. Effects of 'CO' on building material.

3. Effects of 'CO' on plants.

Effects of 'CO' on human beings:

Here dizziness and headache. It is formation of carboxy Hemoglobin in blood.

Hemoglobin reacts with carbon monoxide & produce CO-Hb [carboxy hemoglobin]

$$O_2Hb+CO \rightarrow CO\text{-}Hb+O_2$$

Exposure ML-L^{-1}	**Effects**	**CO-Hb / Hb%**
0-10	No effect	0-2%
10-50	Tiredness	2-10%
50-100	Headache	10-20%
100-200	Mild headache	20-30%
200-400	Savior headache	30-40%
600-800	Increasing pulse rate	50-60%
800-1600	Coma, death	60-70%

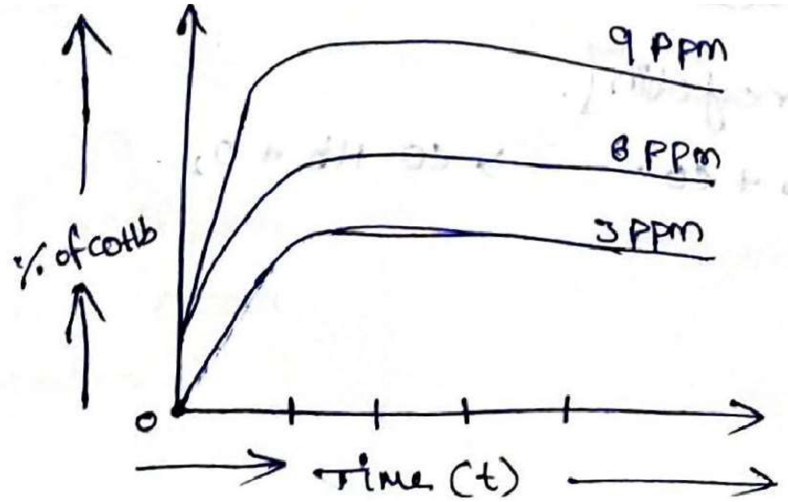
CO is a color less gas, odor less gas. 'CO' is combine with hemoglobin to produce carboxy hemoglobin which restricts transport of oxygen from lungs to cells will the blood stream caring less oxygen, Brain function is affected & heart rate is increases in an attempt to offset the oxygen deficit.

The amount of carboxy Hemoglobin in the blood is normally expressed as the % of saturation level % of CO Hb carboxy hemoglobin is three factors.

1. The carbon monoxide concentration

2. Length of time exposed.

3. Breathing rate control the extent of carboxy hemoglobin in blood.



The above figure represents the relative of carboxy hemoglobin with different exposure times of 'CO' that within 3 to 4 hours carboxy hemoglobin reaches 50% its saturation value.

Effect of 'CO' on building material:-

The building materials are damaged on reacting with carbon compounds. In atmospheric air containing more carbon compounds, these are serious effects on building materials.

Effects of 'CO' on plants:-

In atmosphere air 'CO' levels increases show extreme toxicity towards plants damaging growth vegetation & leaves falling.

Control of 'CO' pollutants:-

The transformation sources are responsible for 74% of all 'CO' emissions & gasoline internal combinations are primary accountable for it. The possible solutions are controlling 'CO' emissions into the atmosphere are,

Modification of internal combination engines to remove the amounts of pollutants formed during fuel combustion by using catalytic convertors. **E.g.:-** 'Pt' catalyst.

The development is exhaust system reactors, which will complete the combustion process.

Development of pollution free power sources to replace the internal combustion engine.

E.g.: - Steam, electric & gas turbines (machine).

Development of substitute fuels for gasoline.

E.g.: - Natural gas in both compressed [CNG] & Liquid fuel gas in both compressed [LNG]

These are used as fuel. Where removing of the pollutants from the process of effluent. We are using the glass, gas cleaning equipment.

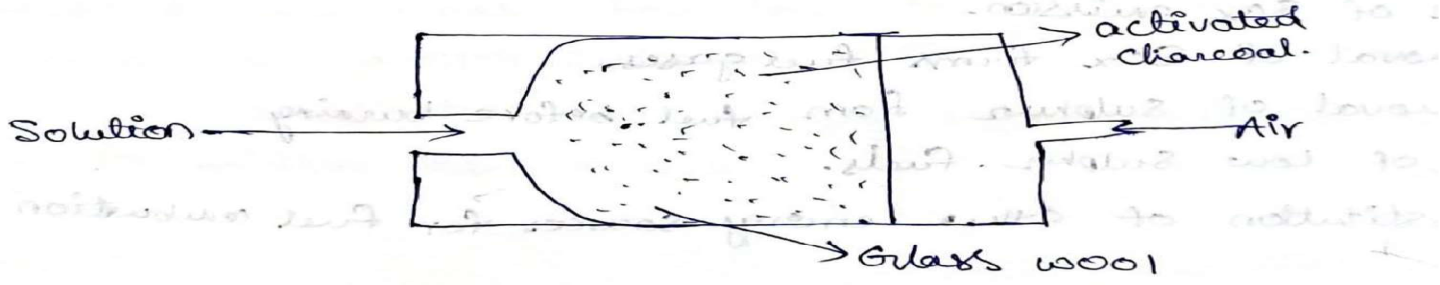
Analysis of 'CO':-

Sampling of gases:-

Sampling & pre concentration:-

A. Adsorption method:-

Adsorption is a surface phenomenon. This phenomenon is used for the sampling & pre concentration of gaseous substances. Active charcoal is an efficient adsorbent for volatile organic compound. After adsorption the charcoal is washed with a suitable solvent, such as 'CS_2' and the solution is analyzed by using the gas chromatography.



Beside the charcoal Al_2O_3, silicate and molecular sieves are also used as adsorbents for H_2 adsorption 'Pd' is used. This is adsorption process is used in purge & trap system. Purge and trap system is a form lead space analysis in which the volatile analyte is trapped on absorbent and then thermally desorbed.

B. Absorption method:-

The other technique for the sampling and pre concentration of gases is absorption phenomenon. We collection are SO_x, NOx, HCl, H_2S, H_2SO_4. This technique is used. Impinges are used for this technique. In this gas is absorbed in a solvent by building the gas through a liquid.

The rate of absorption depends on optimum conditions for efficient sampling are:-

Bubble size small

Temperature low

Pressure more

Concentration is absorbent.

For collection of HF is used water as absorbing solution

For basic gases are used as acid solutions

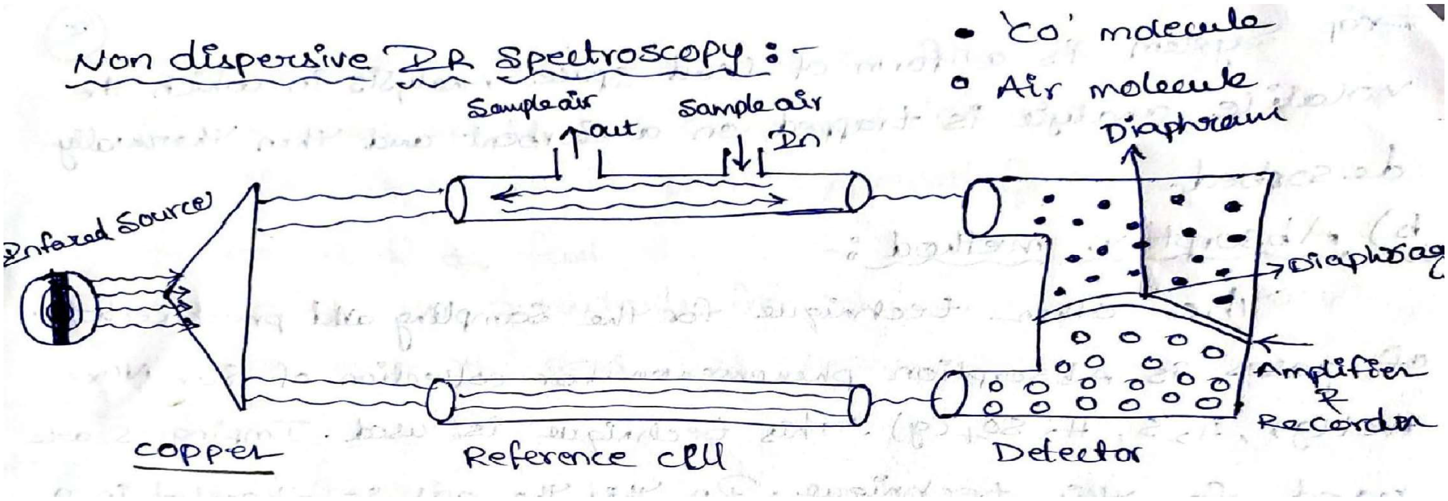
For acidic gases are used as basic solutions

For oils are used as hydro carbons are used

‘CO’ analysis:-

Carbon monoxide [CO] present in air sample it is determined by suing non-dispersive IR spectroscopy and gas chromatography.

Non - dispersive IR spectroscopy:



These IR radiations from the source it not dispersed according to wave length by a prism (or) grating as in a standard IR radiation spectroscopy. Radiation from an IR source chopped by rotating device so that alternatively passes through sample cell and reference cell. Both beams of lights are incident on a detector. This is filled with ‘CO’ gas & divided into two compartments by a flexible diaphragm. The difference in the amount of IR radiation absorbed in two compartments gives rise to temperature of differences , so that the diagram slightly towards one side.

By this method up to 150ppm of ‘CO’ can be measured with a relative accuracy of 5% in the optimum concentration range.

Gas chromatography:-

Mobile phase: - Inert gas or inert solvents.

Stationary phase: - Molecular sieves

Columns: - Packed column

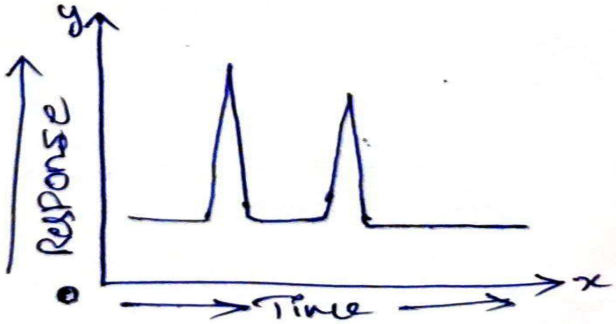
Flow rate: - 1ml for 1min

Detector: - Flame ionization detector

Procedure:-

The sample is fed into the sample loop on a six ports rotator gas sample value. The column contains molecular sieves 5°A at 55°c.

Chromatogram:-



2. Determination of Carbon dioxide (CO_2):-

Sources:-

Here the emission of burning of fossil fuel.

Here emission of deforestation.

Hot springs & Volcanic eruption

Soil: -

When concentration of soil is done CO_2 is released.

Natural sources:-

Natural sources are producing considerable pollutants but in the evolution most of these things are essential components of a balanced ecosystem. These sources are a raised from the naturally.

Forest fires (69%), volcanic eruption (or) action, sulphur springs (gas)**,** marsh gases.

Man made sources:-

These are sources a raised from the man activities.

E.g.:-Motor vehicles (59.5%), Automobiles, burning of coals, burning of fuels. Deforestation, mining, metallurgy, agricultural activities, waste treatment plant, power generation, industrial process (iron, steel, paper, & petroleum industries).

Sinks of CO_2:-

The major sink is the ocean which contains the bulk of dissolved CO_2 as bicarbonate.

Earth surface:-

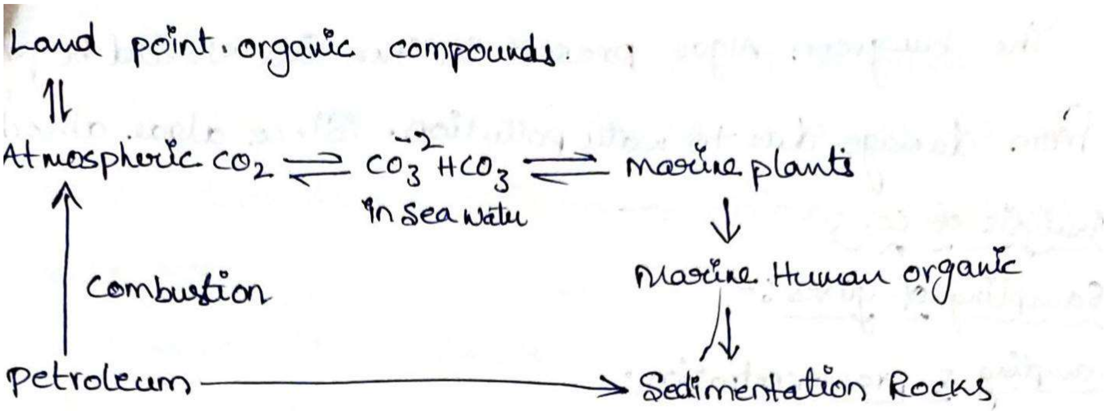
CO_2 is taken by metallic ions present on the earth surface, carbonate compounds are formed water acts as sink of CO_2.

E.g.: -Sea water, river water.

Another important sink is the biomes living green plants in which photo synthesis rate known to accelerate with increase in the CO_2 level.

Reaction:-

CO2 cycle:-



Effects: -

1. Biological effects of CO_2:-

There are several & indirect effects of CO_2 on biological system CO_2 increase the temperature of atmosphere resulting in the increase in the temperature of earths and ocean currents these effects the fishing industries. The increase in the amount of CO_2 in atmosphere causes greater dissociation of sea water .This results in the activity of water. The increase in the concentration of CO_2 in atmosphere increases photosynthesis activity of plants.

2. Effects of CO_2 material:-

Building materials & stones such as limes (or) limestone marbles (polish) absorbs CO_2; acidic substances are formed resulting damages to the material.

3. Effects of CO_2 on human beings:-

Increase in concentration of CO_2 causes respiration problems.

Control of CO_2:-

Since plants absorb a major portion of CO_2 more plants & forests should be grown.

The blue green algae present in the sea should be prevented from damage due to water pollution, since algae absorbs CO_2.

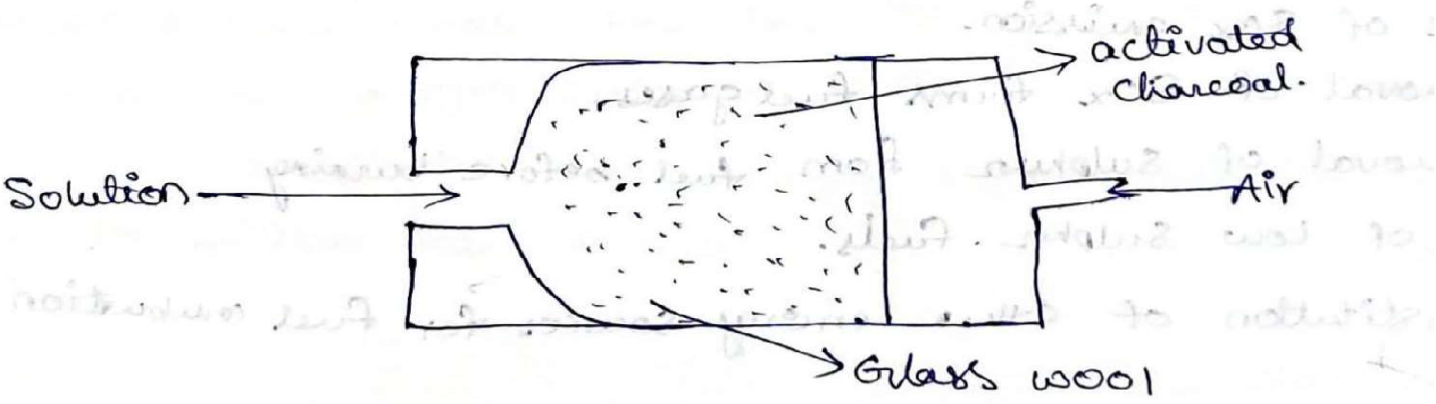
Analysis of ‘CO_2’:-

Sampling of gases:-

Sampling & pre concentration:-

A) Adsorption method:-

Adsorption is a surface phenomenon. This phenomenon is used for the sampling & pre concentration of gaseous substances. Active charcoal is an efficient adsorbent for volatile organic compound. After adsorption the charcoal is washed with a suitable solvent, such as ‘CS_2’ and the solution is analyzed by using the gas chromatography.



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The rate of absorption depends on optimum conditions for efficient sampling are:-

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Pressure more

Concentration is absorbent.

For collection of HF is used water as absorbing solution

For basic gases are used as acid solutions

For acidic gases are used as basic solutions

For oils are used as hydro carbons are used

‘CO_2’ analysis:-

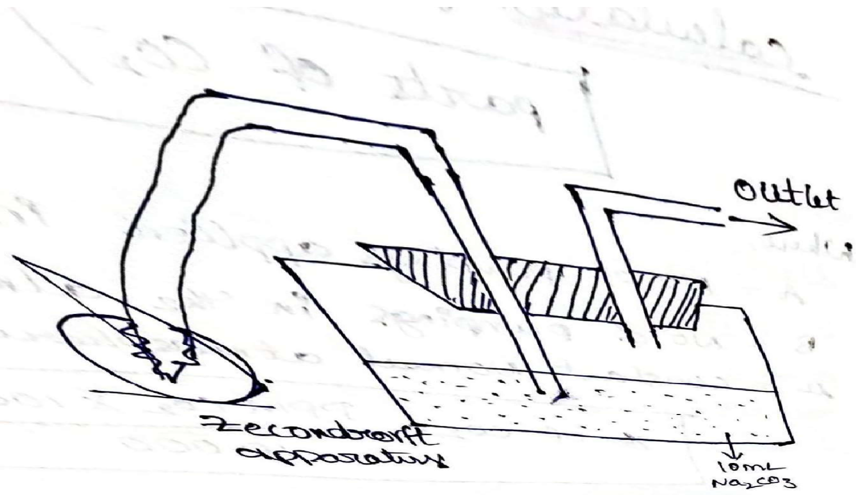
There are two methods for the determination of CO_2.

1. Na_2CO_3 method

2. Hardness portable apparatus

1. Na_2CO_3 method:-

N/10 stock solution of Na_2CO_3 5.3g of Na_2CO_3 / 1L water & add 1g of phenolphthalein solid. It is in pink color.



Procedure:-

Take 0.5ml / min stock solution in 100ml volumetric flask and make up to the mark with water. It is the workable solution Take 10ml of working solution keeps the apparatus in behind the environment. The atmospheric air is pumped through the solution. Now the pump is used to boiling point instrument. The air goes inside this apparatus. Then the air escaped out the outlet & CO_2 present in the atmosphere react with the solution. The Sample solution color changes to pink to color less. By repeat pumping of air the no. of pumping should be noted wash the apparatus again & powered and again we take 10ml of workable solution & repeat the Experiment keep this apparatus in atmosphere. Where the CO_2 analyzed hence repeat the procedure several times until the solution becomes color less. The no of pumping are also noted in 2nd time.

Parts of CO_2^-/ 10,000 parts in air = $\frac{\mu A}{B}$

Where,

A= Number of pumping applied in behind the environment

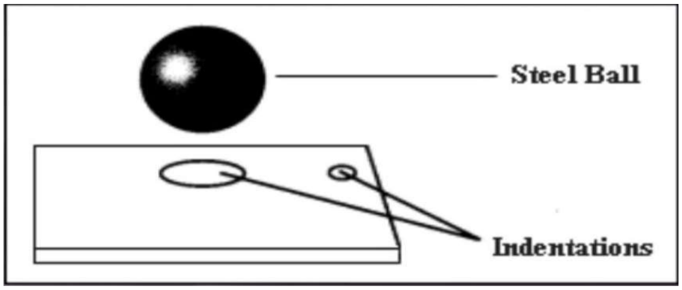
B = Number of pumping in the atmosphere

U = Constant normal atmospheric CO_2 constant.

$$\% CO_2 = \frac{PPM\ CO_2 \times 100}{10,000}$$

2. Hardness portable apparatus:-

Hardness is the resistance of a material to abrasion or localized plastic deformation.



Hardness testing:-

1. Brinell hardness test:-

Here 10mm diameter ball with a load of 500, 1000 or 3000kg.

2. Rockwell hardness test:-

A cone shape indenter, the depth of penetration is measured.

3. Vickers hardness test:-

The pyramid shape indenter.

Theory:-

Hardness is a measure of the resistance of a metal to permanent (plastic) deformation.

The hardness of the metal is measured by loading is into its surface.

The material which is usually a ball, pyramid, or cone, is made of a material much harder than the material being tested.

There are two types of hardness – temporary hardness and permanent hardness.

Temporary hardness – also called ‘Carbonate hardness.

Permanent hardness also referred to as ‘non-carbonate hardness is the hardness due to the presence of calcium or magnesium sulfates, chlorides and nitrates.

Hardness is a measure of how much a material resists changes in shape. Hard things resist pressure.

Some examples of hard materials are diamond, boron carbide, quartz, tempered steel, ice, granite, concrete.

Ability of material to resist wear, tear, scratching, abrasion cutting is called hardness.

ii) Sulphur compounds:-

1. Sulphur dioxide (SO_2)

2. Sulphur trioxide (SO_3)

3. Hydrogen sulphide (H_2S)

1. Determination of Sulphur dioxide (SO_2):-

Sources:-

Man made sources:-

These sources contribute 33% of SOx pollution annual worldwide emission from these sources are 14 bands 1.5×10^{-6} these respectively among man made sources.

From fuel combustion-74%

Industries-22%

Transporatations-2%

Oxides of sulphur mainly enter into the atmosphere by natural process mostly by volcanic provides 67% of SOx pollution. The combustion of any sulphur containing material will produce sulphur dioxide.

$$S+O_2\rightarrow SO_2$$

$$SO_2+O_2\rightarrow SO_3$$

Atmospheric SO_2 mainly comes from burning of fossil fuels in industries metallurgical furnaces.

Thermal power plants and petroleum refineries, SO_2 present in the atmosphere converts into SO_3, sulphur oxide enter into the atmosphere through manmade activities, volcanic explosion decay to organic material, containing sulphur biological reduction of sulphur results in the emission of H_2S into atmosphere, H_2 is converts into SO_2 by oxidation process.

Reaction of SOx:-

The atmospheric reaction of SO_2 depends on the concentration & the presence of other gases humidity light intensity, temperature.

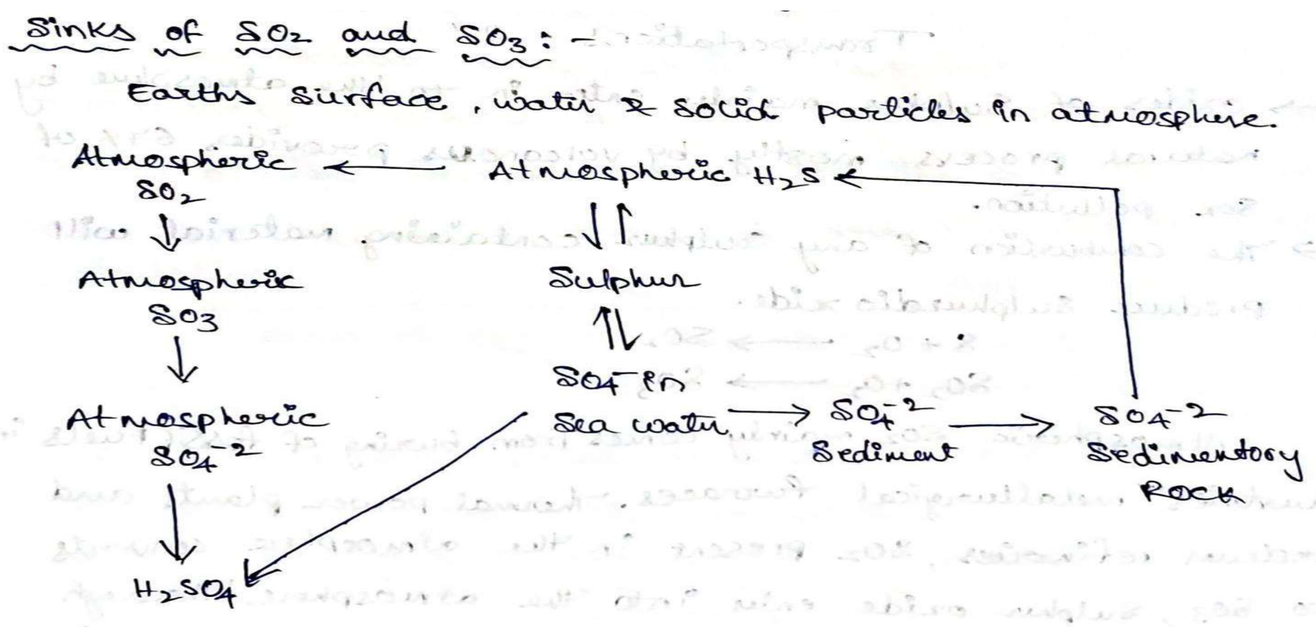
Photo chemical reaction of SO_2:-

Photo chemical dissociation at 218nm is given by,

$$SO_2+h\nu\ (\lambda\leq218) \rightarrow SO + O$$

The natural sunlight the rate of conversion of SO_2 to SO_3 is faster than reaction rate is darkness, SO_2 converts to SO_3 & finally to sulphate.

Sinks of SO_2 and SO_3:-



Acid rain:-

SO_2 also causes acid rain SOx enters into the atmosphere & converts to H_2SO_4.

$$SO_2 + 1/2\ O_2 + H_2O \rightarrow H_2SO_4$$

H_2SO_4 combined with HCl to generate acidic precipitation is widely known as acid rain. This acid rain damage to building & sculptural material of marble, limestone etc...

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + CO_2 + H_2O$$

Effects:-

SO_2 in air causes irritation to the mucous membrane. SO_2 effects not only man & plants and building materials but also effect on paper. It can even dissolve nylon paper also absorbs SO_2, which will oxidized to H_2SO_4 causing the paper to come brittle & fragile.

SO_2 polluted air accelerated the corrosion rates of metals such as Fe, Zn, Cu, steel.

Effects of human beings:-

SO_2& other oxides sulphur cause ageing & lung disease

Exposure $mL.L^{-1}$	Effects
0-10ppm	No effect
10-40ppm	Headache
40-100ppm	Noise effect
Above 100ppm	Lungs damage
Above 200ppm	Kidney failure
More than 300ppm	dead

Effects of SO_2 on building material:-

Building materials are damaged on reacting with sulphur compounds. In atmospheric air containing more sulphur compounds savior effect on building material.

Effect of SO_2 on plants:-

In atmosphere air 'SO' levels increases show extremes toxicity towards plants damages the leaves of plants.

Control of SO_2:-

These are four possible approaches to the remove fuel & control of SOx emission. Remove of SOx forms fuel gases.

The removal of sulphur compounds from before burning the fuel. The use of low sulphur fuels.

The substitution of other energy sources is used for fuel combustion.

SOx forms fuel gases can be conveniently eliminates by using chemical scrubbers. The fuel stock gases are passed through slurry of lime stone, $CaCO_3$, which absorbs SO_2 quite sufficiently.

$$2CaCO_3 + 2\ SO_2 + O_2 \rightarrow 2\ CaSO_4 + CO$$

An alternative process is based on a relation b/w HSO_3^- ions (from SO_2) & citrate ions; the fuel gas is cooled to 50°C lower free from particulates & trace of H_2SO_4.

$$SO_2 + H_2O \leftrightarrow HSO_3^- + H^+$$

$$HSO_3^- + H_2\ cit \leftrightarrow [HS{:}O3\ H_2cit]$$

Analysis of SO_2:-

Sampling of gasses:-

Sampling & pre concentration:-

A. Adsorption method:-

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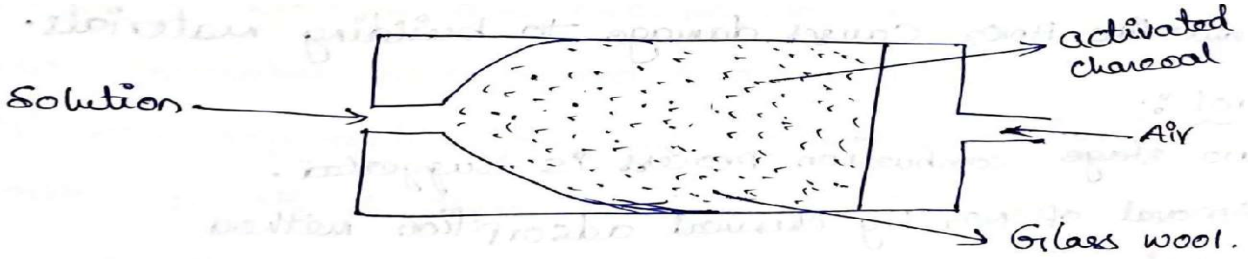

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For oils are used as hydro carbons are used

SO_2 analysis:-

It is done by two methods

1. Conductometric method

2. West – Geake Spectrophotometric method

1. Conductometric method:-

It has been the gases of commercial continuous SO_2 analyzers. Since 1929, SO_2 is collected in H_2O_2 solution and the increased conductance of H_2SO_4 solution is measured.

$$SO_2+H_2O_2 \rightarrow H_2SO_4$$

2. Spectrophotometric method: - West- Geake spectrophotometric method:-

Standard Test Methods for Sulfur Dioxide Content of the Atmosphere (West-Geake Method) Sulfur dioxide is a major air pollutant, commonly formed by the combustion of sulfur-bearing fuels.

Principle:-

SO_2 is collected in a scrubbing solution containing $HgCl_4^{2-}$; the scrubbing solution contains [$HgCl_2$ + KCl / NaOH]. The solution is allowed to react with HCHO (formaldehyde) commonly known as methanol and then with pararosaniline hydrochloric acid ($C1_9H_{18}ClN_3$). The red-violet dye is formed, and then absorbance is measured at 548nm.

Reactions:-

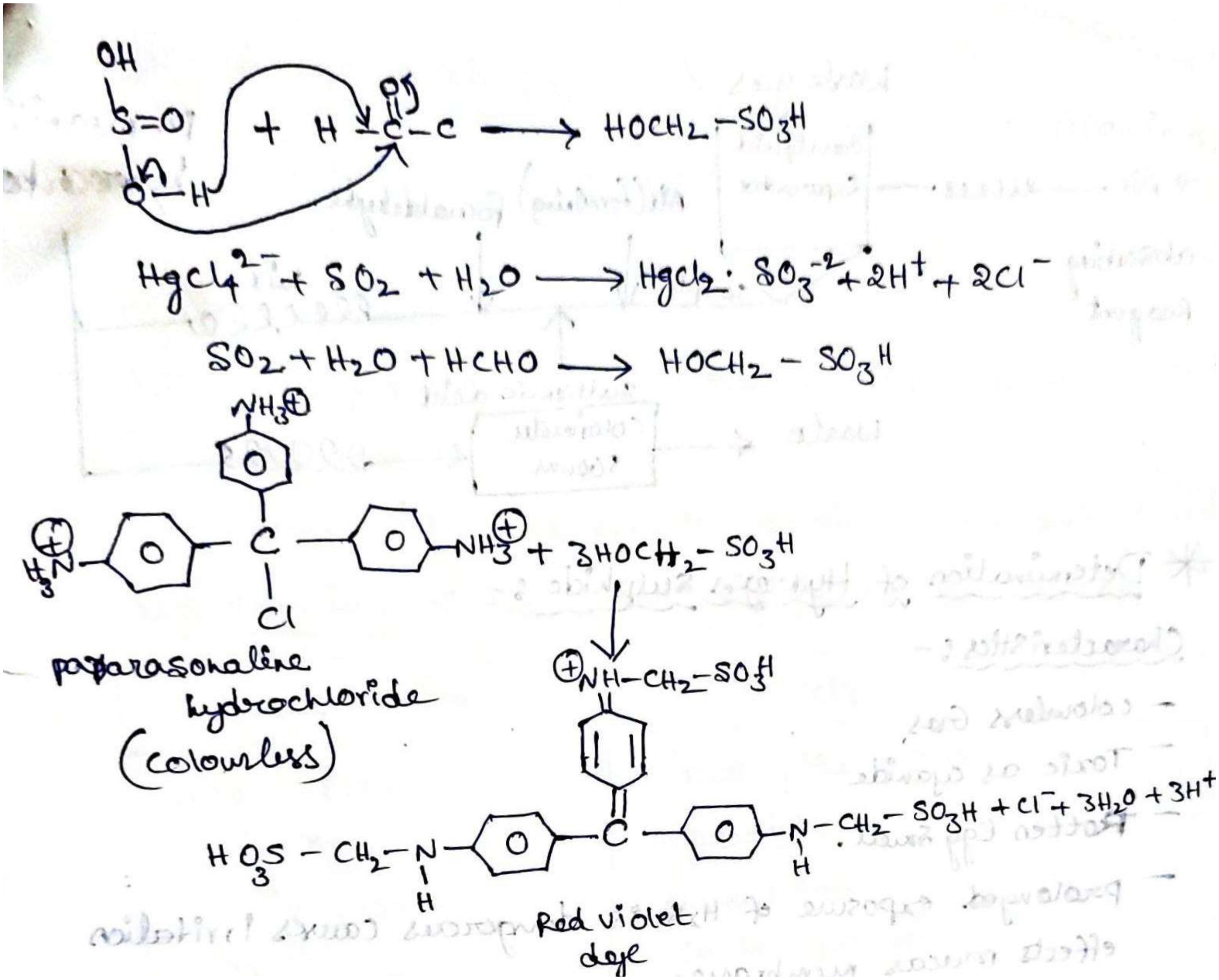
1. Tetrachloromercurate II is produced by adding two moles of NaOH (or KCl) to1 mole of $HgCl_2$.

$$2NaOH + HgCl_2 \rightarrow 2Na+ + [HgCl_4]^-$$

2. Sulphur dioxide is trapped & Stabilized through complexion.

$$SO_2 + HgCl_4] + 2H_2O \rightarrow HgCl_2\ SO_3 + 2H^+ + 2Cl^-$$

3. Formation of the colour product, pararosaniline methyl sulfuric acid.



Chemical required:-

Sample [30-60 L air], Scrubbing solution [13.6 $HgCl_2$ –7.5g KCl / NaOH →1L]

HCHO (formaldehyde), Pararosanilline [4ml of 1% aqueous solution acidic with 6ml of conc. of HCl]

Procedure:-

Pump 30-60 L of air through 10ml of scrubbing solution [13.6 $HgCl_2$ –7.5g KCl/NaOH→1L] in a sample impinge at 1-2L min-1, then add 1ml of dilute pararosaniline hydrochloride reagent solution [4ml of 1% aqueous solution acidic with 6ml of conc. of HCl] and diluted to 100ml water & 1ml of 0.2% HCHO solution, after 20-30 min color solution is measure the absorbance at 548nm**.**

Convert the volume of air sampled to the volume at standard conditions of 25^0C, 760mm Hg.

$$\mathbf{V_R = V \times \frac{P}{760} \times \frac{298}{(t+273)}}$$

Here,

V_R=Volume of air at 25^0C & one atmosphere

V=Volume of air sampled, liters

P=Barometric pressure, mm Hg

t=Temperature of air sampled

Determine the conc. of sulphur dioxide in the sample by the following formula is,

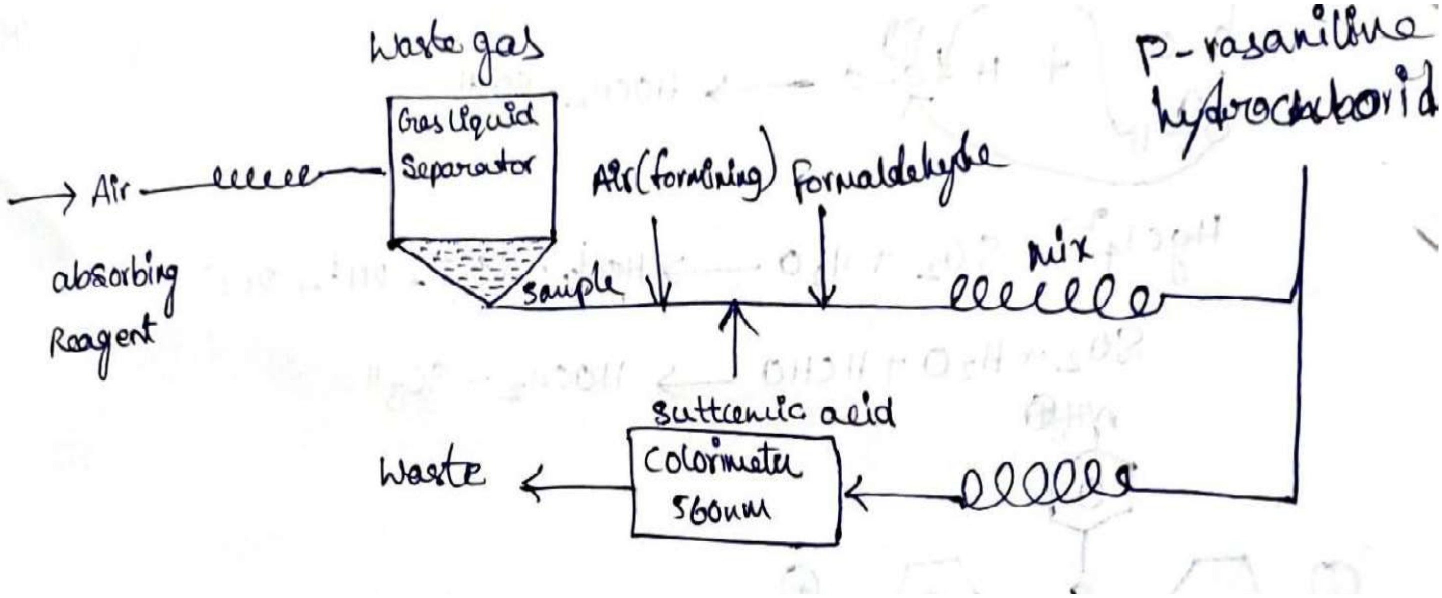
SO_2, $\mu g/m^3 = W/V_R$

Here,

W=$\mu g SO_2$/10ml found from calibration curve, 10^3= conversion of liters into m^3.

Where desired, values maybe reported in ppm

PPM $SO_2 = \mu g SO_2/m^3 X 3.82 X 10$-4



3. Determination of Hydrogen sulphide (H_2S):-

Characteristics:-

Colorless gas, Cyanide as a toxic

Rotten egg small- Hydrogen sulfide is a colorless, flammable gas that smells like rotten eggs at low concentration levels in the air. It is commonly known as sewer gas, stink damp, and manure gas. Prolonged exposure of H_2S is dangerous cause's irritation effects mucous membrane.

Sources:-

1. Natural sources:-

Decaying vegetation & animal material, anaerobic bacteria attacks sulphates in sediments & convents in to H_2S.

2. Industrial source:-

Use of high sulpha fuels, petroleum refineries, craft paper mills, tannery wastes, industrial water in stagnant water swamps & other areas where bacterial action reduces sulphur compounds to hydrogen sulphide. It is estimated that decaying organic matter in the world emits to million turns of H_2S.

Reaction of H_2S in air:-

$$H_2S+O_3 \rightarrow H_2O+SO_2$$

Effects of H_2S:-

They cause's the headache.

H_2S rapidly passes through the membrane of the lungs & penetrates into blood.

H_2S reacts with lead paints to from lead sulphide causing discoloration of the paint the paint turns black.

Concentration	**effects**
Up to 5ppm	Destroy the appetite
10ppm	Headache
50-100ppm	Characteristic eye damage caused by eye
150ppm	Irritation of mucous membrane
320-500ppm	Diarrhea , bronchitis problems pneumonia
700-1000ppm	Fatal death due to respiratory failure

Control of H_2S:-

These are four possible approaches to the remove fuel & control of SOx emission.

Remove of SOx forms fuel gases. Here the removal of sulphur from fuel of before burning.

The use of low sulphur fuels.

The substitution of other energy sources is used for fuel combustion.

SOx forms fuel gases can be conveniently eliminates by using chemical scrubbers. The fuel stock gases are passed through slurry of lime stone, $CaCO_3$, which absorbs SO_2 quite sufficiently.

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$$SO_2 + H_2O \leftrightarrow HSO_3^- + H^+$$

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Analysis of H_2S:-

Sampling of gases:-

Sampling & pre-concentration:-

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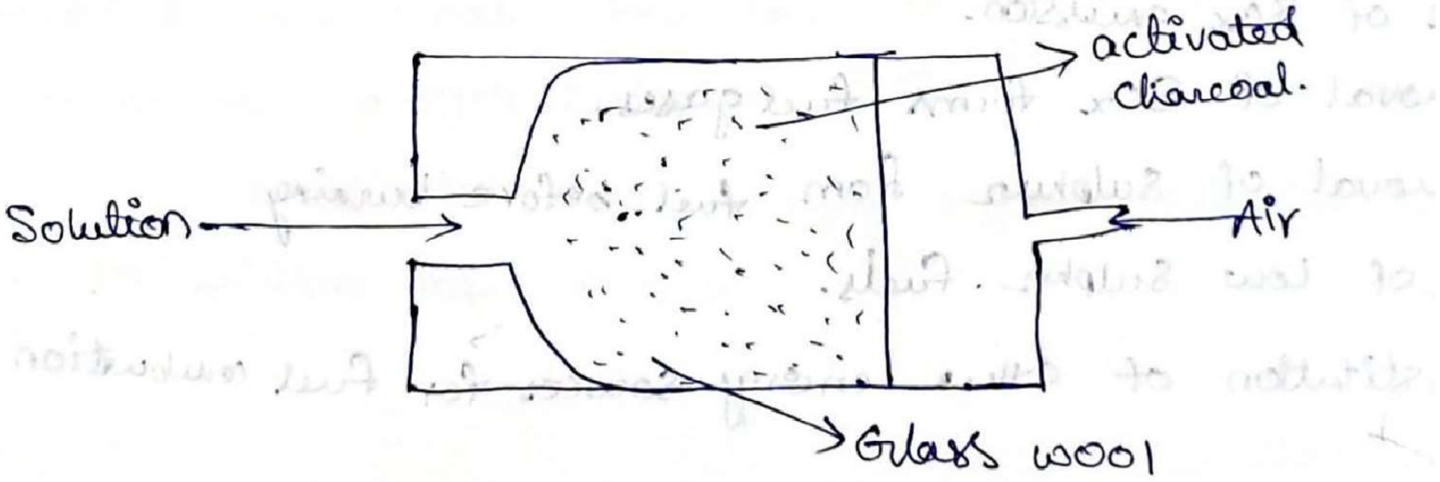

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For collection of HF is used water as absorbing solution

For basic gases are used as acid solutions

For acidic gases are used as basic solutions

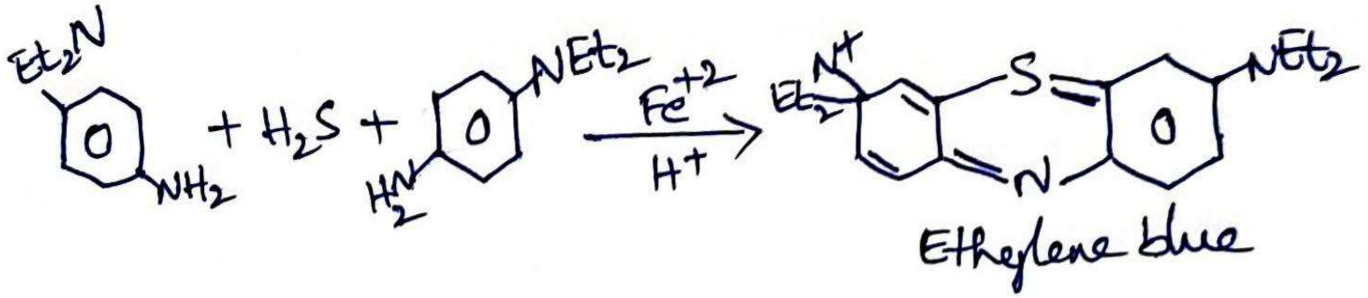
For oils are used as hydro carbons are used

Analysis hydrogen sulphide:-

Spectrophotometric method:-

Principle:-

The main principle involved in analysis of H_2S in (N-N$^|$ diethyl p-phenylenediamine) react with H_2S to produce colored substances measure the absorbance at 670mm.



Chemicals required: - Sample [10-15L air]**, [**$3CdSO_4.8H_2O$-NaOH=mix air]**,** $NaClO_4$**,** N-N$^|$ diethyl

P-phenylenediamine, [H_2SO_4**-**(NH_4) SO_4=Fe (III)], $CHCl_3$.

Procedure:-

Transfer 500ml of a 1% of solution of $3CdSO_4.8H_2O$ & 500ml of 0.01m NaOH solution to a standard gas wash bottle with filtered, glass disposer pump 100-500 lit of air at 10-15lit through the wash bottle and 2ml of 1ml $NaClO_4$& shake well. Next add 1ml of 2% w/v N-N^1 -diethyl P-phenylenediamine in 50% w/v H_2SO_4& 1ml of a filtered 10% w/v solution of Fe (III) ammonia sulphate dissolved in 1m H_2SO_4 often 10 mines. Transfer the solution to a separating funnel extract & make up to 25ml measure the absorbance ad 670mm.for calibrate curves use a stack solution of NO_2S prepared by washing the crystals with ethanol & drying on filter papers.

iii). Nitrogen compounds:-

1. Nitric oxide (NO)

2. Nitrogen dioxide (NO_2)

Oxides of nitrogen are NO, N_2O, NO_2, N_3O_3, N_2O_5.

Here atmosphere in 95% NO & 5% of NO_2.

It NOx represents nitric oxide (NO) and nitrogen dioxide (NO_2).

1. Determination of Nitric oxide (NO):-

Nitric oxide is a molecule that's produced naturally by your body, and it's important for many aspects of your health. NO is a colourless gas 'NO' enter into the atmosphere by lightening & biological process at higher temperature favors formation of 'NO' internal combustion engine produce 'NO' combustion of fuels in furnaces are also the sources of 'NO' emission.

Reaction of 'NO':-

Average life of 'NO' is 4 days in unpolluted atmosphere. In the atmosphere 'NO' is oxidized to 'NO_2'. The conversion of NO-NO_2 in ambient air involves the oxidation of organic substances initiated by free radicals of (:OH). The oxidation of alkaline initiated by (:OH) radical, where 'NO' is converted to NO_2 alkyl peroxide radical results with 'NO' and from R-O-NO_2.

Uses in human body:-

Nitric oxide is produced by nearly every type of cell in the human body & one of the most important molecules for blood vessel health. It's a vasodilator, meaning it relaxes the inner muscles of your blood vessels, causing the vessels to widen. In this way, nitric oxide increases blood flow & lowers blood pressure.

Determination of Nitrogen dioxide (NO_2):-

Nitrogen dioxide is a chemical compound with the formula NO_2. It is one of several nitrogen oxides. NO is an intermediate in the industrial synthesis of nitric acid, millions of tons of which are produced each year for use primarily in the production of fertilizers. At higher temp, it is a reddish-brown gas.

Elevated levels of nitrogen dioxide can cause damage to the human respiratory tract & respiratory infections and asthma. Long-term exposure to high levels of nitrogen dioxide can cause chronic lung disease. Reaction of NO_2 in atmosphere: NO_2 exists as dimmer, N_2O_4, NO_2 reactive and important species.

Reaction of NO_2 in atmosphere:-

NO_2 exists as dimmer, N_2O_4, NO_2 reactive and important species. (140°C, 150°C – 600°C)

$$N_2O_4 \rightarrow 2NO_2 \rightarrow 2NO_2 + O_2$$

Reaction with OH:-

$$NO_2 + :OH \rightarrow HNO_3$$

Reaction with ozone:-

$$NO_2 + O_3 \rightarrow NO3^* + O_2$$

$$NO_2 + O_3 \rightarrow NO + O_2$$

NO_2 is react with R-O & R – O_2 & form addition compounds.

Sources of oxides of nitrogen (NOx):-

Oxides of nitrogen are formed by the action of cosmic rays in upper atmosphere.

These are formed by the combustion of coal, oil, natural gas and gasoline.

These are formed by products in some chemical industries.

NO is the main production of combustion, N_2 is automobile exhaust. NO is oxidized to NO_2.

Source of NO_2:-

Oxides of nitrogen are NO, N_2O, N_3O_3, N_2O_5.

Here atmosphere 95% NO & 5% of NO_2.

It NOx represents as nitric oxide and nitrogen dioxide.

Power plants & other energy conversion system are the sources of NO_2, automobiles exhaust also contains NO_2.

Effect of oxides of nitrogen:-

Effects of human beings:-

NO & NO_2 are potentials of health hard. NO_2 is four times toxic than 'NO'. Effects of the hemoglobin level 100 ppm of NO_2 exposure causes in information of lung tissues 200ppm causes bronchitis 1000ppm causes lung damage, so Silo-filler's disease is a chemical pneumonitis from exposure to oxides of nitrogen. These gases are produced within hours & sometimes up to two weeks after fresh plant material is placed in silos disease, NO_2 has irritating effects on mucus membrane, headache, coughing Effects on plants.

NO_2 cause high damage to plants 1000ppm exposure causes leaf spotting & break of plant tissues,10ppm exposure of 'No' decreases the photo synthesis.

Effects on plants:-

NO_2 causes high damage to plants 1000ppm exposure causes leaf spotting & breaks of plant tissues; 10ppm exposure of 'NO' decreases the photo synthesis.

Effects on materials:-

Here 2ppm level fades the colours of textile materials, oxides of N_2 have no direct affection on building materials, and the secondary pollutant like HNO_3 causes damages to building materials.

Control:-

Two stage combustion processes is suggested. The removal of NOx is chemical adsorption method. By using catalytic conversion we can remove the NOx from automobile emission.

The NOx emissions from non power plants can be reduced by burning the fuel at relatively low temperature in excess air under this condition NO is not found.

NOx emissions from stock gas can be removed by chemical adsorption process using H_2SO_4 or alkaline scrubbing solution containing $CaCO_3$ & Mg $(OH)_2$. NO is converted into N_2O_3 which is easily absorbed.

$$NO_2+NO\rightarrow N_2O_3$$

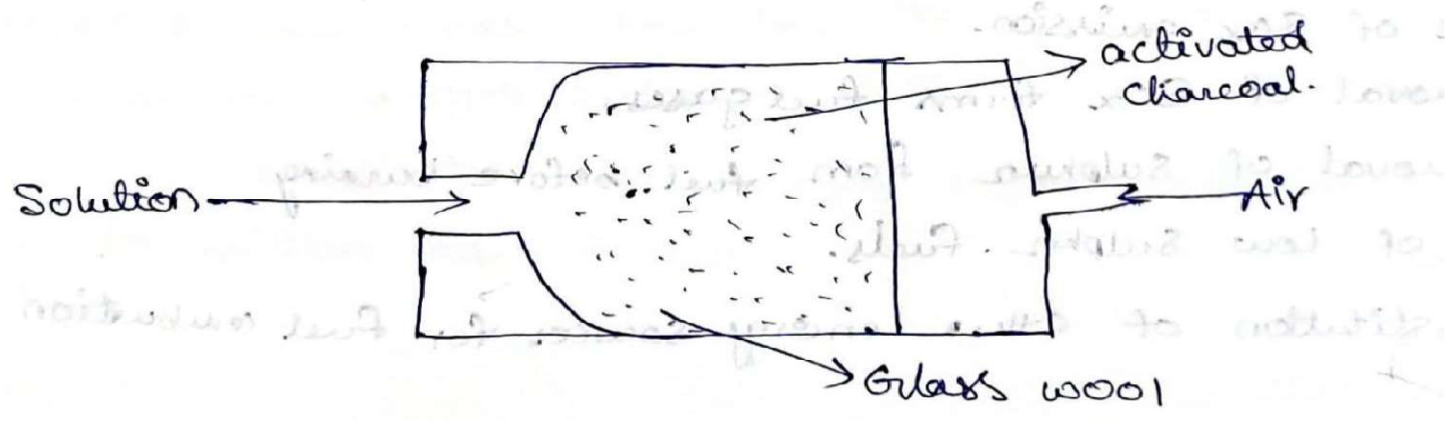
Analysis of NO_x:-

Sampling of gasses:-

Sampling &pre concentration:-

A. Adsorption method:-

Adsorption is a surface phenomenon. This phenomenon is used for the sampling & pre concentration of gaseous substances. Active charcoal is an efficient adsorbent for volatile organic compound. After adsorption the charcoal is washed with a suitable solvent, such as 'CS_2' and the solution is analyzed by using the gas chromatography.



Beside the charcoal Al_2O_3, silicate and molecular sieves are also used as adsorbents for H_2 adsorption 'Pd' is used. This is adsorption process is used in purge & trap system. Purge and trap system is a form lead space analysis in which the volatile analyte is trapped on absorbent and then thermally desorbed.

B. Absorption method:-

The other technique for the sampling and pre concentration of gases is absorption phenomenon. We are collection of SO_x, NOx, HCl, H_2S, and H_2SO_4. This technique is used. Impinges are used for this technique. In this gas is absorbed in a solvent by building the gas through a liquid.

The rate of absorption depends on optimum conditions for efficient sampling are:-

Bubble size small

Temperature low

Pressure more

Concentration is absorbent.

For collection of HF is used water as absorbing solution

For basic gases are used as acid solutions

For acidic gases are used as basic solutions

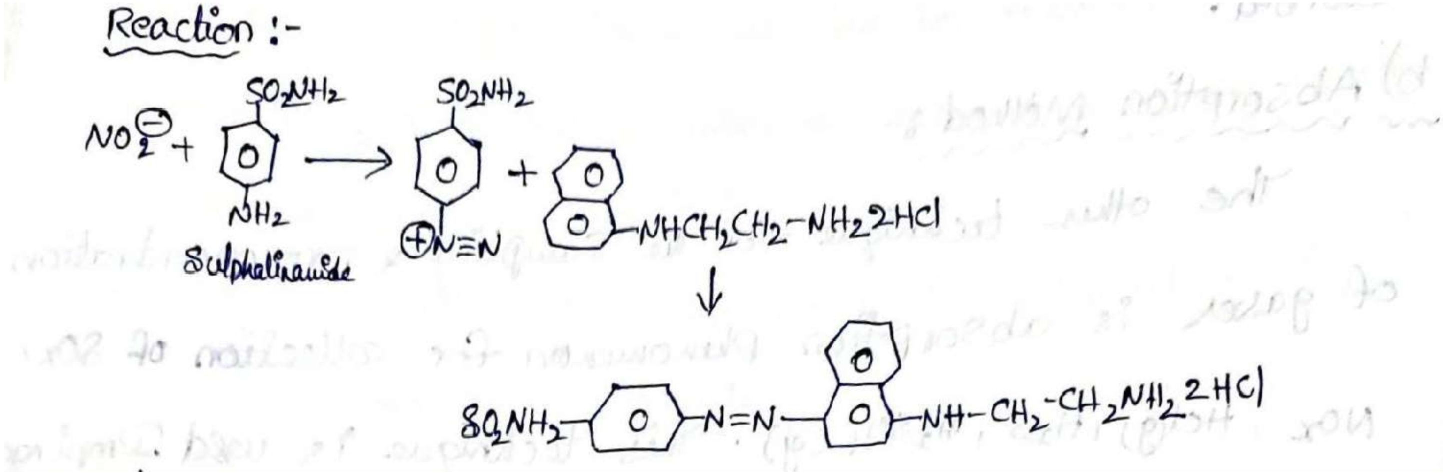
For oils are used as hydro carbons are used

NO_x analysis:-

Spectrophotometric method:-

The air sample is passed through NaOH solution. Then the produced NO_2 is reacting with H_3PO_4, sulphanilamide, and NEDA. The resulting reddish purple azodye absorbance is measured at 534nm. It is employed for NO_2 at 0.012 -1.5 µg NO_2/ ml.

Reaction:-



Preparation of solutions:-

Preparation of NaOH:-

Dissolve 4g of NaOH in one liter distilled water.

Preparation of sulphanilaminde:-

Mix 20g of sulphanilamide & 50ml of conc. of H_2SO_4 & 700ml of water and mixed well, make up to the mark with one liter with distilled water.

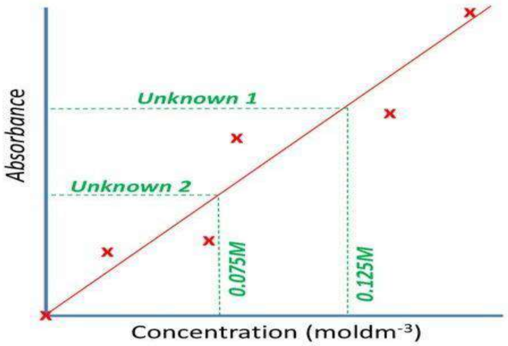
Procedure:-

Air sample is collected through a 50ml absorbing reagent at 200ml/min for 24hrs. To take aliquot solution & then to this added 1ml H_2O_2, then remove of SO_2 interference 10ml sulphanilamide & 1.1 ml of NEDA with thoroughly mixed, after one hour then to form an azodye absorbance is measure at 543nm against a reagent blank.

Graph:-On x-axis is taken into a concentration.

On y-axis is taken into an absorbance.

Finally we get an unknown 'A & B' absorbance's values.



iv) Hydrocarbons:-

A hydrocarbon is an organic chemical compound composed exclusively of hydrogen and carbon atoms. Hydrocarbons are naturally-occurring compounds and form the basis of crude oil, natural gas, coal, and other important energy sources.

Aliphatic hydrocarbons:-

Aliphatic hydrocarbons are hydrocarbons based on chains of C atoms. There are three types of aliphatic hydrocarbons. Alkanes are aliphatic hydrocarbons with only single covalent bonds. Alkenes are hydrocarbons that contain at least one C–C double bond, and Alkynes are hydrocarbons that contain a C–C triple bond.

Polycyclic Aromatic hydrocarbons:-

Aromatic hydrocarbons have a special six-carbon ring called a benzene ring. A polycyclic aromatic hydrocarbon is a hydrocarbon—a chemical compound containing only carbon and hydrogen—that is composed of multiple aromatic rings. The group is a major subset of the aromatic hydrocarbons.

1. Determination of Aliphatic hydrocarbons:-

Hydrocarbons are the most simple organic component formed atmosphere .they are considered as a primary pollutants. The hydrocarbons are form from secondary pollutants.

E.g.: - Photo chemical smog.

Sources:-

Methane is an important compound of natural gas. Methane is produced by decomposition of organic matter is presence of anaerobic bacteria line n the sediments of wet leads and water & soil.

$$2(CH_2O) \rightarrow CO_2 + CH_4$$

Methane is produced from other sources, animals, rice, paddies, permanganate, hydrocarbons enters into atmosphere from automobiles. Certain point emits hydrocarbons. Aromatic hydrocarbons constitutes of particulate matter. The aromatic hydrocarbons enter into air by chemical industries.

Atmospheric reaction of hydrocarbons:-

Photo chemical reactions are remove hydrocarbons from atmosphere.

$$NO_2 + h\nu \rightarrow NO + O:$$

$$CH_3CHO + h\nu \rightarrow :CH_3 + H:CHO$$

$$C_4H_{10} + O \rightarrow :C_4H_4 + :OH$$

$$C_4H_9 + O_2 \rightarrow C_4H_9OO:$$

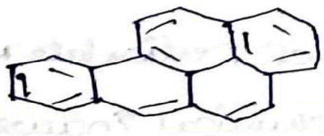
$$C_4H_9OO: \rightarrow \text{methyl ethyl ketone} + :OH$$

Hydrocarbons undergo heterogeneous reactions dust compound of metal oxides & charcoal are having a catalytic effect on y oxidation of hydrocarbons.

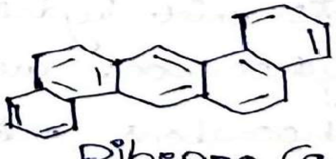
2. Determination polycyclic aromatic hydrocarbons [PAH]:-

Particles from combustion of fossil fuels contain polycyclic aromatic hydrocarbons, Aromatic hydrocarbons are classified as benzene derivates & multiple ring derivatives, multiple ting derivatives is also called as polycyclic aromatic hydrocarbons.

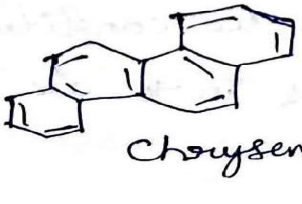
Due to the burning of fossil fuel PAH enters in to the atmosphere. PAH other PCAH are entered into the atmosphere by motor vehicle exhaust smoke, combustion of coal in electric generating plants, the PAH react with HNO_3, NO_2 & O_3 under atmospheric conditions. Then produces a new PCAH formed in atmospheric are chrysene, benzo (a) pyrene, benzo (a, b), anthracite, fluroanthracene.



a
Benzo (aromatic
Pyrene [BAP]



Dibenzo (a,b) anthracene
[DBA]



Chrysene

Reaction of PAH in atmosphere:-

1. Photo oxidation:-

Polycyclic hydrocarbons are formed in soot particles. In the presence of light PAH undergo oxidation forming oxygenated products.

2. Ozonalysis:-

PAH reacts with ozone & forms addition compounds carboxy PAHs are formed.

3. Nitration of PAH:-

Polluted ambient air contains oxides of N_2. They act as nitrating agents for PAH. The nitro PAH undergo photo decomposition forming quinines & phenol derivatives.

Effects:-

Impacts of human life:-

The Irritation of mucous membrane. They eye irritation. Lung takes place due to high concentration**.**

Impacts of plant life:-

Here yellowing & occasional narcosis of leaves.

Here Chlorosis of floral buds.

The inhibition of terminal growth. Shortening of inter nodes.

Here thickening of stems in plants. Acetylene & propylene at 50-500ppm show extreme toxicity towards plant damages growth of generation.

Control:-

Control of fuel efficient engines, the released hydrocarbons into the atmosphere can be removed by several chemical & photochemical reactions.

They are thermodynamically unstable towards oxidation & tend to be oxidized to CO_2 & the other solid organic particulate matter.

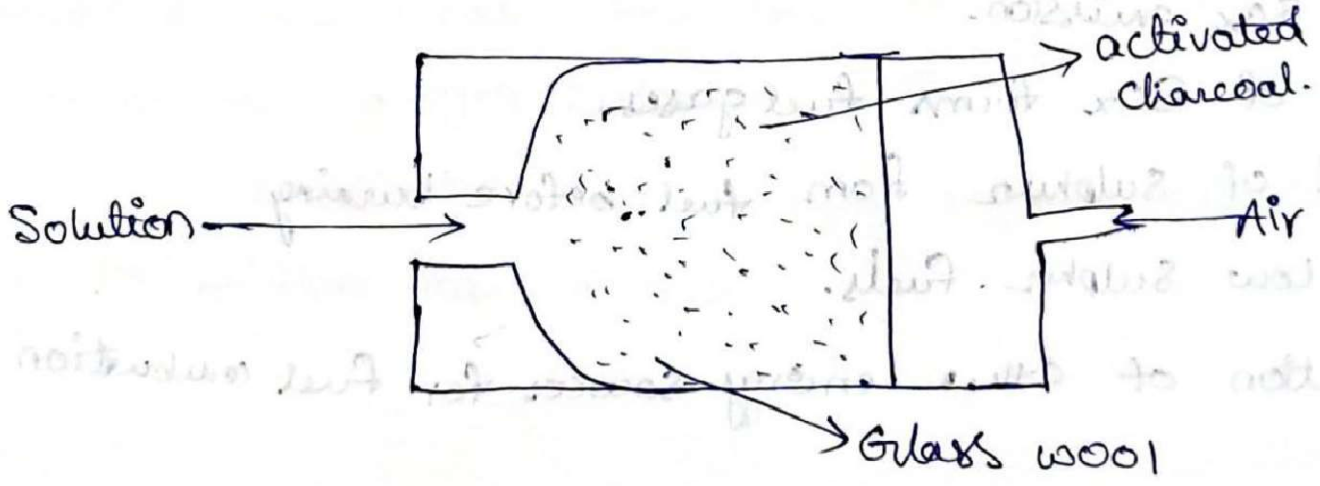
Analysis of 'Hydrocarbons':-

Sampling of gases:-

Sampling & pre concentration:-

A. Adsorption method:-

Adsorption is a surface phenomenon. This phenomenon is used for the sampling & pre concentration of gaseous substances. Active charcoal is an efficient adsorbent for volatile organic compound. After adsorption the charcoal is washed with a suitable solvent, such as 'CS_2' and the solution is analyzed by using the gas chromatography.



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Pressure more

Concentration is absorbent.

For collection of HF is used water as absorbing solution

For basic gases are used as acid solutions

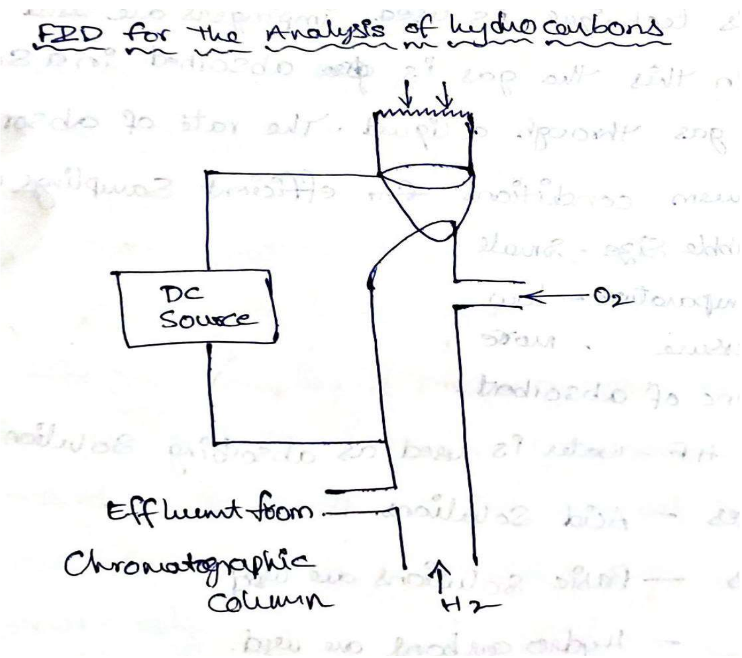
For acidic gases are used as basic solutions

For oils are used as hydro carbons are used

Hydrocarbon analysis:-

Hydrocarbon can be conveniently connected in an absorption column packed with a very porous styrene divinely benzene polymer. Air is sampled out the rate of 4L / min. The absorbed gas is separated by heating the columns.

Then the desorbed gas is analyzed by gas chromatography by using FID, during the burning of hydrocarbons in Flame, carbon ions are formed & those are collected at their respective electrodes. The Resulting current is proportional to the no. of carbon in hydrocarbons.



v) Particulate matter:-

Particulate matter is the sum of all solid and liquid particles suspended in air many of which are hazardous. This complex mixture includes both organic and inorganic particles, such as dust, pollen, soot, smoke, and liquid droplets.

i) Repairable & suspended particulate matter:-

Small solid particles & liquid droplets are collectively formed as particulate matter. The size of the particulate matter is very important. The size is in the range of 0.1—10µm. The clean air the particulate mass level ranges from 10µg/m^3-60µg/m^3. In particular air mass level range is 60-200µg/m^3 in the suspended particulate matter of 0.001µ.

Sources:-

Here volcanic eruptions. The blowing of dust & they soil by the wind. Here spraying of salt & other solid particles by the seas & oceans.

Man made sources:-

They fly ash from power plants, smelting & mining operations. Smoke from in complete combustion process.

Effects or impacts:-

Particles like aerosol enter into the lungs & cause asthma, cancer. The toxic metals like As, Pb, Be, etc present in particulate matter show harmful effects on animals. Particulates such as dust & soot deposited on the plant leaves retarded the rate of photosynthesis.

Air bone particles including soot, dust & mist damage the variety of materials. Particulate cause corrosion of metals & the damage of buildings sculptures, paints etc. Smoke & fumes tend to increase the atmospheric turbidity and reduce the visibility of sunlight.

Control of particulate matter:-

Removal of particles by using suitable filters,

By spraying water,

By using electrostatic precipitations then charged particles.

ii) Inorganic particulate matter:-

Sources: -

The burning of fuels contains metals.

E.g.: - Fe_3O_4 particulate is formed during the combustion of pyrite containing coal.

$$3\,FeS_2 + 8SO_2 \rightarrow Fe_3O_4 + 6SO_2$$

SO_2 is oxidized to H_2SO_4 & converted into mists is known as aerosol.

$$SO_2 + 1/2(O)_2 + H_2O \rightarrow H_2SO_4$$

In the presence of basic air pollutants such as NH_3 (or) CaO are formed.

$$H_2SO_4 + 2NH_3 \rightarrow (NH_4)2SO_4$$

$$H_2\,SO_4 + CaO \rightarrow CaSO_4 + H_2O$$

Here decomposition of lime stone then to form a CaO.

$$CaCO_3 \rightarrow CaO + CO_2^{|}$$

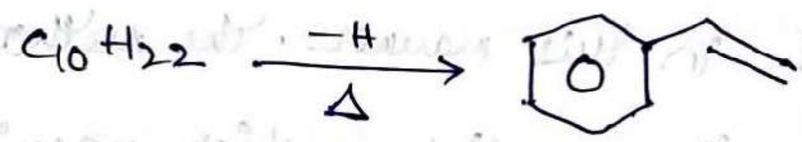
iii) Organic particulate matter:-

Sources:-

Burning of fossil fuels leads to formation of organic particulate matter.

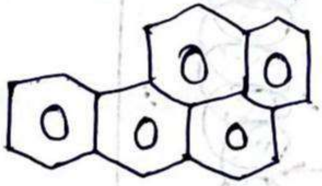
Polycyclic (polynulear) aromatic hydrocarbons (PAH) in organic particulate matter are known as the carcinogenic effect. Among there benzo- alpha-Pyrenees is well known.

Higher molecular weight paraffin is paralyzed to yield $C_{10}H_{22}$ which undergoes further pyrolysis.

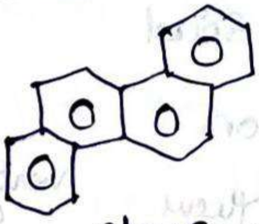


polycyclic aromatic hydrocarbons.

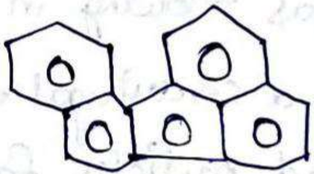
PAH such as chrysene, benzo (Alpha) pyrene, Benzo fluroanthracene are important organic particulate matter.



Benzo(α)pyrene

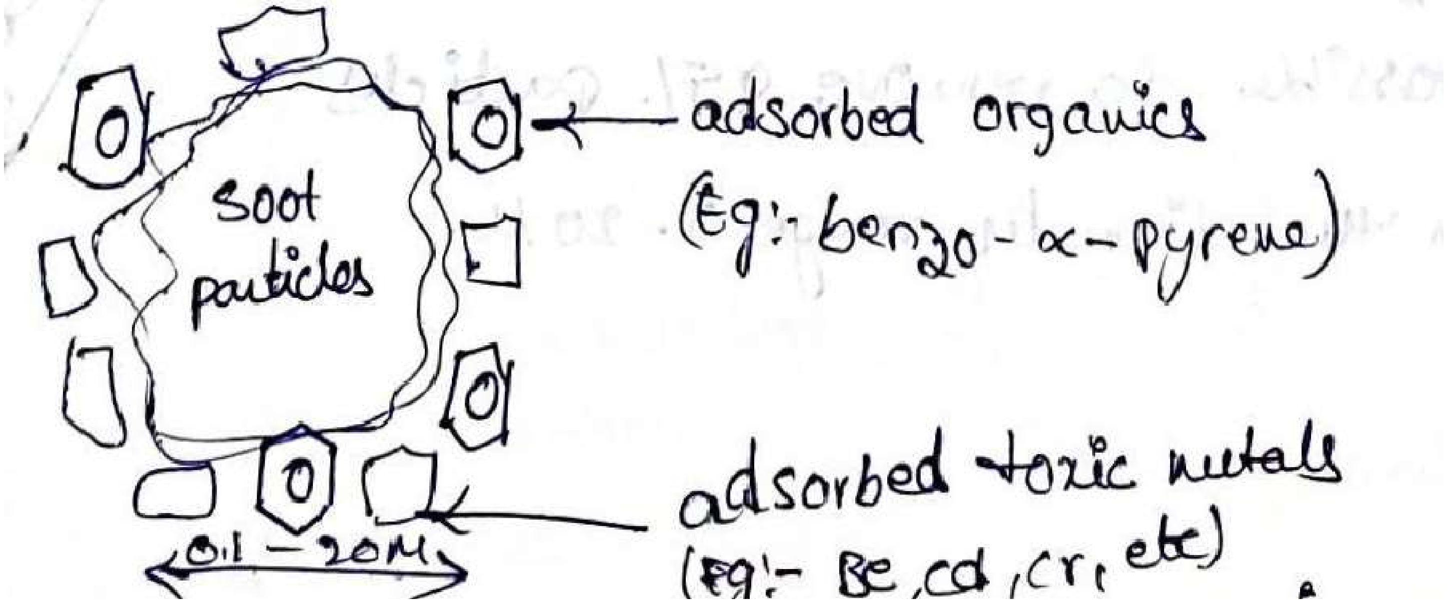


Chrysene



Benzofluoranthene.

PAH compounds remain adsorbed on the soot particles along with metals like Be, Cr, Cd etc... Soot particles containing absorbed toxic metals & organic carcinogens.



Control of particulate emission:-

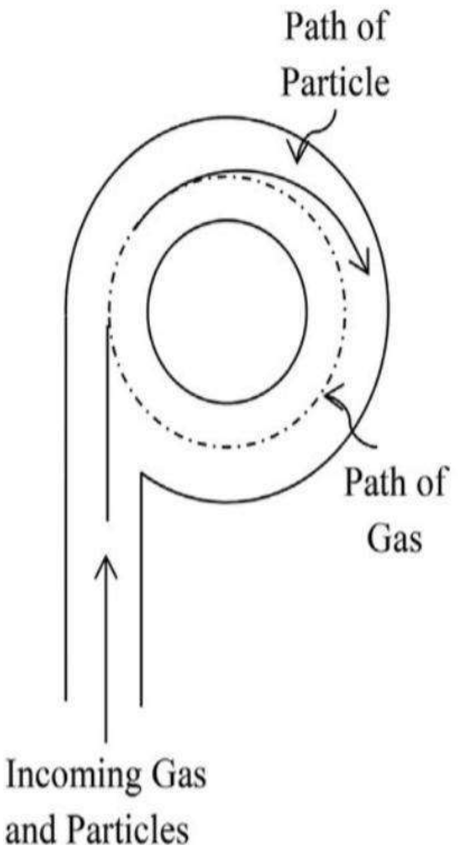
The removal of particulate matter from gas streams is an essential step for air pollution control. These are four types of equipments used for this purpose.

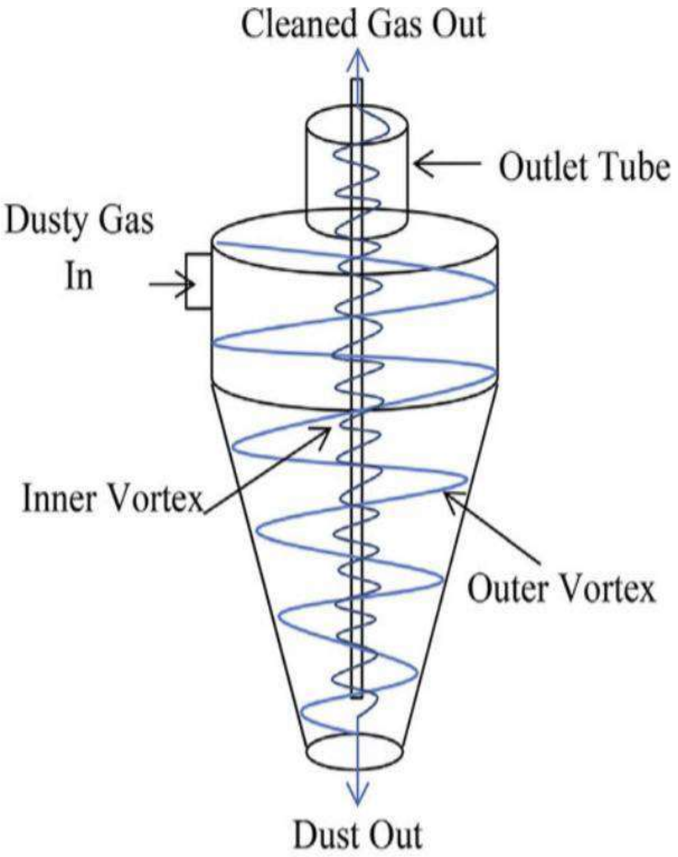
1. Gravity setting chamber:-

Effluent gases are led into a chamber. This is large enough to permit gas velocities to decrease & dust or droplets to settle. The chamber is generally in the shape of a horizontal rectangle tank. Article with a diameter more than 50μ are ordinarily removed in this manner. The method is how ever not suitable for fine particles, which require longer setting time.

2. Cyclone collector:-

A gas flowing in tight spiral produces a centrifugal force on suspended particles, forcing them to move outward through the gas stream to a wall. They are collected. Thus it is possible to remove 95% particles in the diameter range 5-20 μ.





3. Wet scrubber:-

These utilize a liquid (usually H_2O) to help remove solid, liquid or gaseous contaminants. The extent to contact & interaction are increased by the use of spray chambers or towers. The liquid is introduced into gas stream as fine spray.

4. Electrostatic precipitators:-

An electrostatic precipitator is a filter less device that removes fine particles, like dust and smoke, from a flowing gas using the force of an induced electrostatic charge minimally impeding the flow of gases through the unit.

These are based on the principle that aerosol particles acquire changes when subjected to an electrical field.

$$F=Eq$$

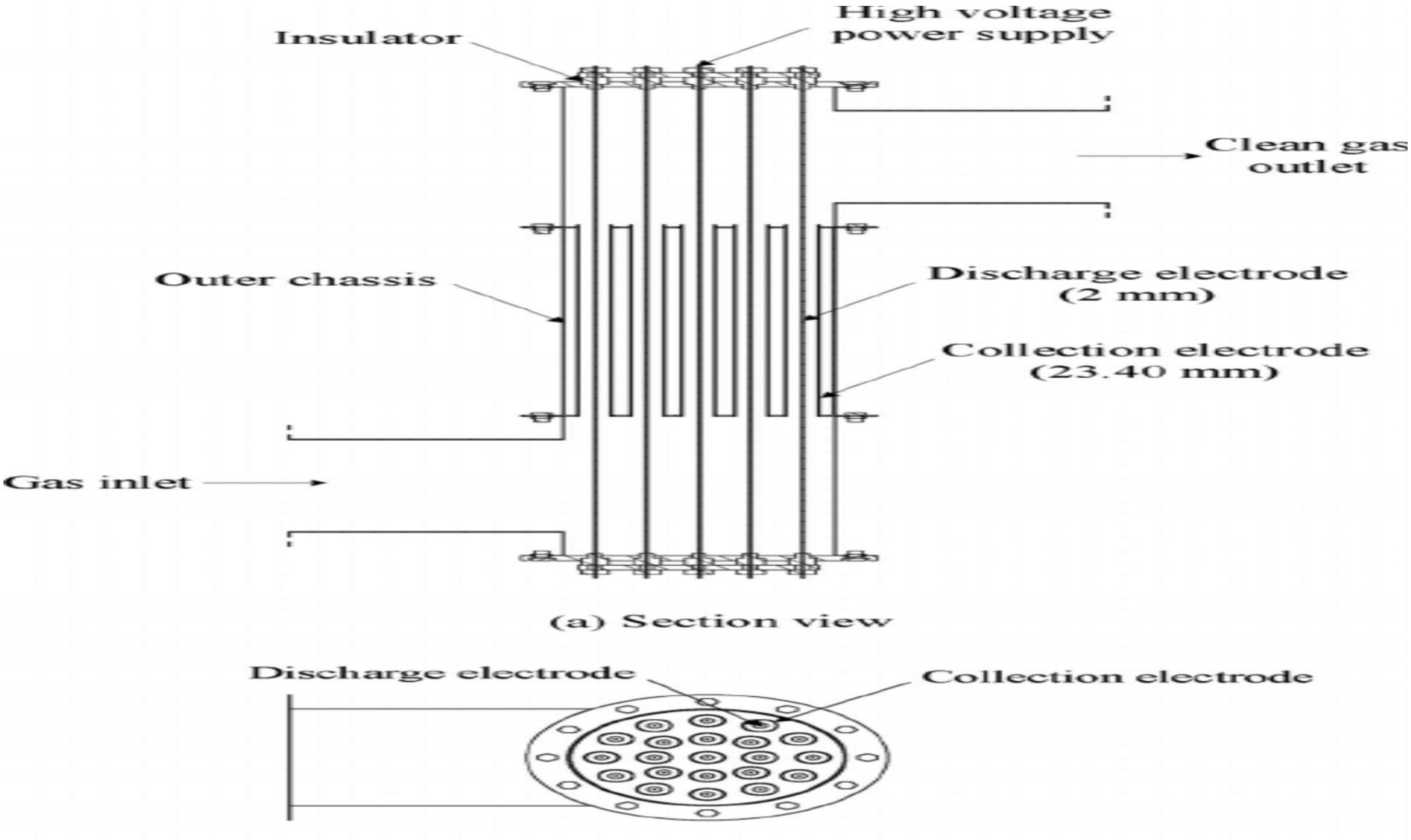
Where,

F= Force in dynes to which the particles are subjected.

E= Voltage gradient (volt/cm)

q= Electrostatic change on the particles

The particles acquires a change is led through a high voltage dc-corona. The changed particles are attached to a grounded surface from which they are removed ozone is the possible product of the corona discharge.



(a) Section view

(b) Top view

Analysis of particulate matter:-

Three methods are used in the analysis of a particulate matter.

1. Filtration method

2. Electrostatic precipitation method.

3. Gravitational method

Filtration is standard method.

1. Filtration method:-

Filtration is the most common technique for sampling the particulate method is filtered by the following filter paper.

Cellulose filter paper--- for metals & anions

Glass fibers----- organic compounds

Silica filters------trace inorganic species.

For the environmental health point of view samples are collected from the places where the people are working for this region.

Light weight battery operated pumps are used. These pump the air at two liters per minute through a 3-7cm glass fiber for 8hours. From polluted air samples are collected at different points & are analyzed samples are collected by filters.

This technique in this the gas is observed in a solvent by bumbling the gas through a liquid. These absorbs used are of various types. They are impinges counter current scrubbers, packed columns & twitted glass, scrubbers the rate of adsorption depends are,

Bubble size small

Temperature low, Pressure more

Concentration is absorbent.

For collection of HF is used water as absorbing solution

For basic gases are used as acid solutions.

Procedure:-

Before sampling maintain the filter at 15-30°c at 50% relative humidity for 24 hours. Then take its weights, fit the filter to the high volume sample & draw air through a 406-5cm^2 portion of the filter at a rate of at least 1.7m^3 as measured by rotometer. After sampling for 24hr, remove filter paper & equilibrate for 24 hrs weight the filter calculate the amount of particulate matter per unit volume of air. Particulate matter from the filter may be extracted with a suitable solvent or digested by oxidizing acid mixture before elemental analysis.

Pre weight of filter paper = W_1

Weight of filter paper + particulate matter = W_2

Weight of particulate (W) = $W_2 - W_1$

Mass concentration = $W/V \ \mu g/m^3$

Soot particles:-

Soot is formed as a residue on combustion of fuel in power plants & automobiles. It accounts for 50% of the particulate load in urban areas. Chemically it is highly condensed product of polynuclear aromatic hydrocarbons. It contains large no of aromatic rings. Because of its large surface are. Soot acts as a carrier for toxic organics.

E.g.: - Benzo (alpha) pyrene, Toxic trace metals (Be, Cd, Cr, Mn, Ni, V etc.)

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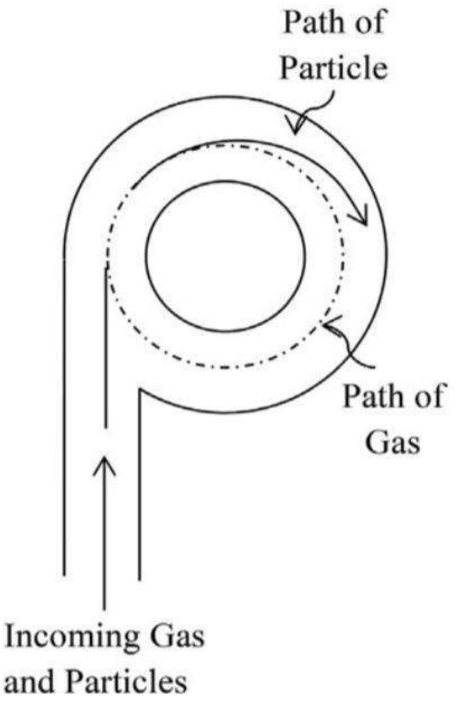

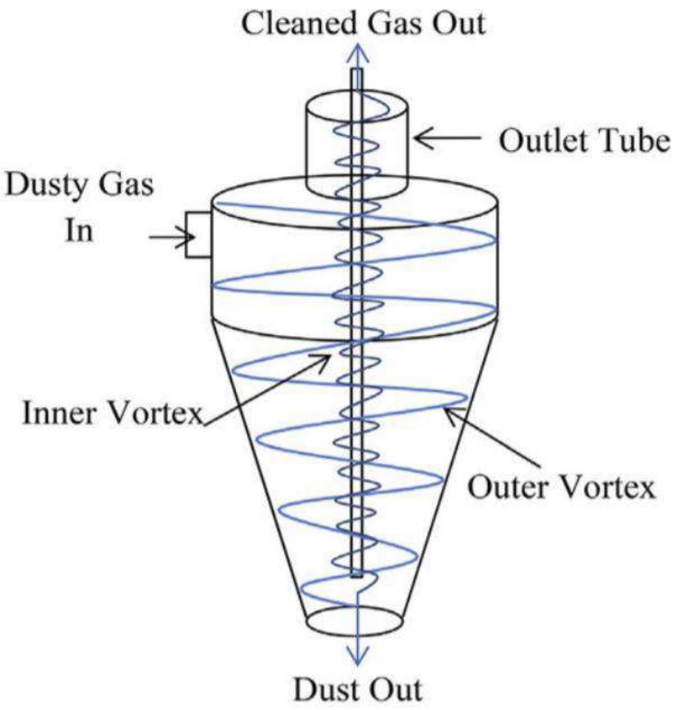

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b) Secondary pollutants:-

Primary pollutants react with one another (or) they may react with water vapor in presence of sunlight to form an entirely new product. The secondary air pollutants are products of photo chemical reaction both ozone & PAN are products of photochemical smog.

The secondary air pollutants are following:-

1. PAN (peroxy acetyl nitrate)

2. PBN (peroxy benzyl nitrate)

3. Ozone (O_3)

1. PAN (peroxy acetyl nitrate):-

Source:-

PAN's are secondary pollutants, which are mean they are not directly emitted as exhaust from power plants (or) internal combustion of engines for they formed from the other pollutants by chemical reactions of atmospheric free radicals of reaction catalyzed by ultraviolet light from sunlight unbounded hydrocarbons by aldehydes, ketones & di carbon compounds. Whose secondary reactions create peroxy acetyl radical, which combine with nitrogen dioxide to form PAN? The most common acetyl radical is formed from the free radical oxidation of acetaldehyde, various ketone (or) photolysis of dicarbonyl compounds such as methyl glyoxalin (or) di acetyl.

Free radicals are highly reactive chemical species that are formed by the photo dissociation of several inorganic & organic compounds.

E.g.: - Hydroxyl radicals, ketoens, aldehydes, PAN, H_2O_2, nitrous acid & nitric acid.

Formation of PANs:-

PANs are powerful respiratory, eye irritants present in photochemical smog. They are formed from peroxy acetyl radical & nitrogen dioxide.

$$\text{Hydrocarbons}+O_2+NO_2+\text{light}\rightarrow CH_3COONO_2$$

The general equation is,

$$CxHyO_3 + NO_2 \rightarrow CxHyO_3NO_2$$

Reactive hydrocarbons (those with C=C) from auto exhaust interact with O_3 to form a hydrocarbon free radical $RCH{:}_2$.

$$\text{Hydrocarbons} + O_3 \rightarrow RCH{:}_2 \rightarrow \text{Hydrocarbon radical } (RCH{:}_2)$$

$RCH{:}_2$ rapidly react with O_2 to from another free radical $RCH_2O{:}_2$.

$$R\text{-}CH{:}_2 + O_2 \rightarrow RCH_2O{:}_2$$

$RCH_2O{:}_2$ reacts with 'NO' to produce NO_2 the free radical $RCH_2O{:}$.

$$RCH_2O{:}_2 + NO \rightarrow RCH_2O{:} + NO_2$$

This new free radical next interact with O_2 to yield a stable aldehyde (RCHO) and hydro peroxy ($HO{:}$)

$$RCH_2O{:} + O_2 \rightarrow RCHO$$

$HO{:}_2$ then reacts with another molecule of 'NO' to give NO_2 & $HO{:}$.

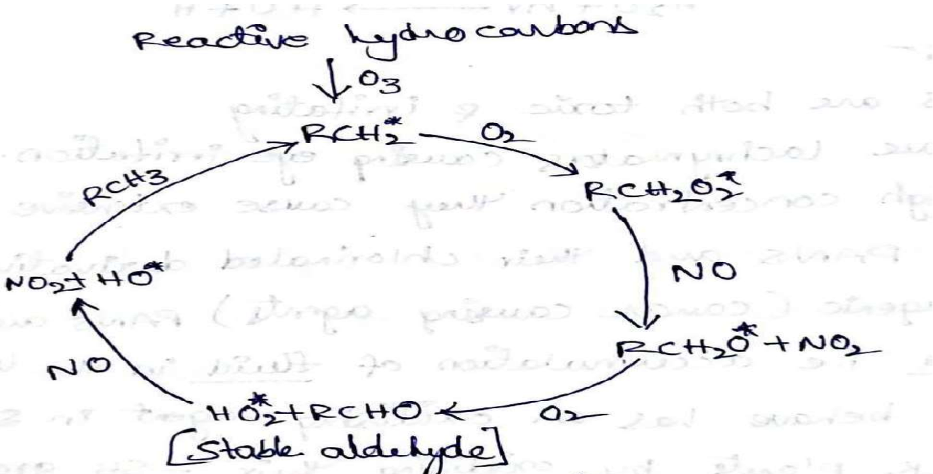
$$HO{:}_2 + NO \rightarrow NO_2 + HO$$

$HO{:}$ extremely reactive & rapidly reacts with stable hydrocarbons RCH_3 to yield H_2O regenerate. The hydrocarbon is a free radical $RCH{:}_2$. There by completing cycle, this goes & on as a chain reaction .One complete cycle yield two molecules of NO_2, one molecule of aldehyde (RCHO) & generate the free radical ($RCH{:}_2$) to start all over again soon there is a rapid build up to smog products..

$$HO{:} + RCH_3 \rightarrow H_2O + {:}RCH_2$$

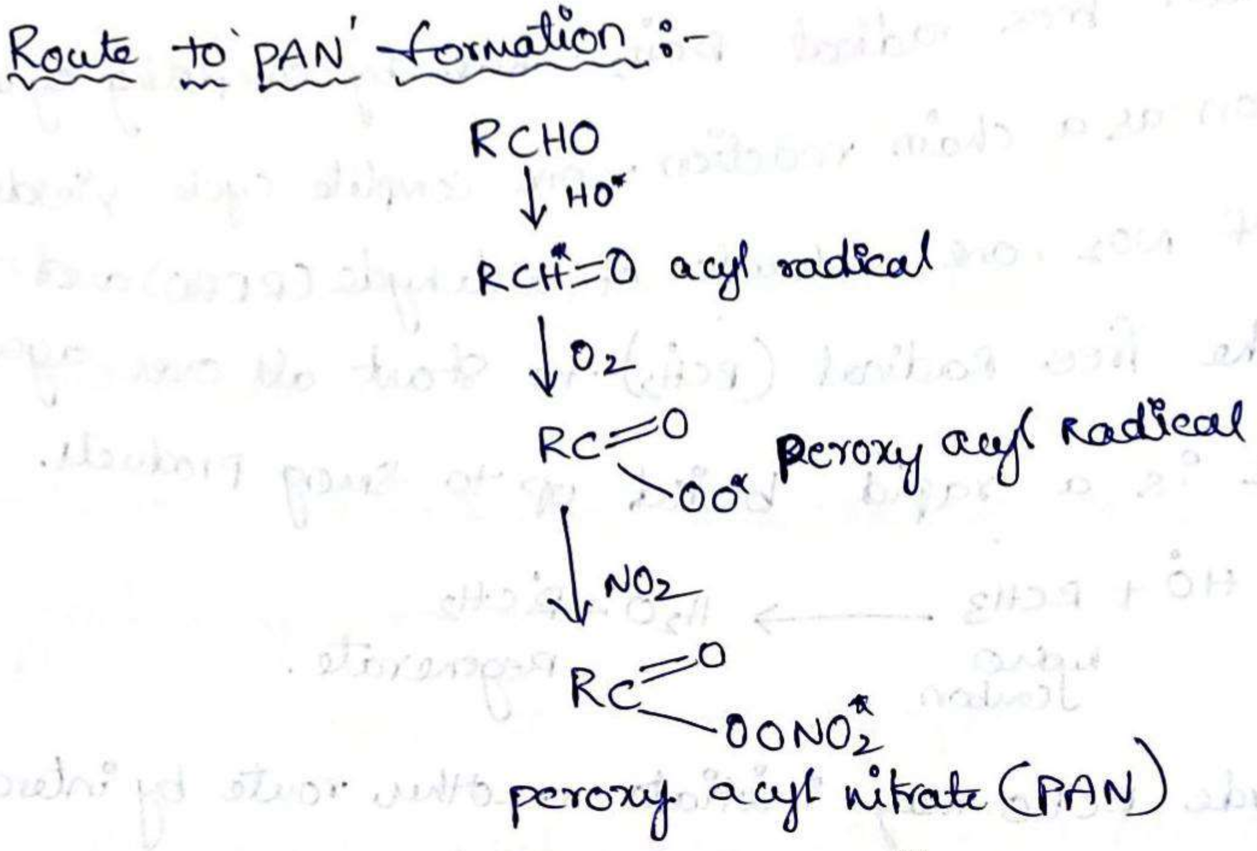
The aldehyde RCHO may initiate another route by interaction with $HO{:}$ radical leading to formation of an acyl radical RC=O, peroxy acyl radical R $COO{:}_2$ (by reaction with O_2) and finally PAN (by reaction with NO_2).

$$RCHO + {:}OH \rightarrow RC{=}O + RCOO{:}_2$$



Smog formation Reactions.

Route to PAN formation:-



PAN formation Reactions

Hydroxyl radical HO* is the single most independent reactive intermediate species in atmospheric chemical process. It is formed by several mechanisms at higher attitudes it is produced by photosynthesis of water.

$$H_2O+h\nu\rightarrow HO{:}+H$$

Effects:-

PANs are both toxic & irritating. They are lachrymators causing eye irritation. At high concentration they cause extensive damage to vegetation.

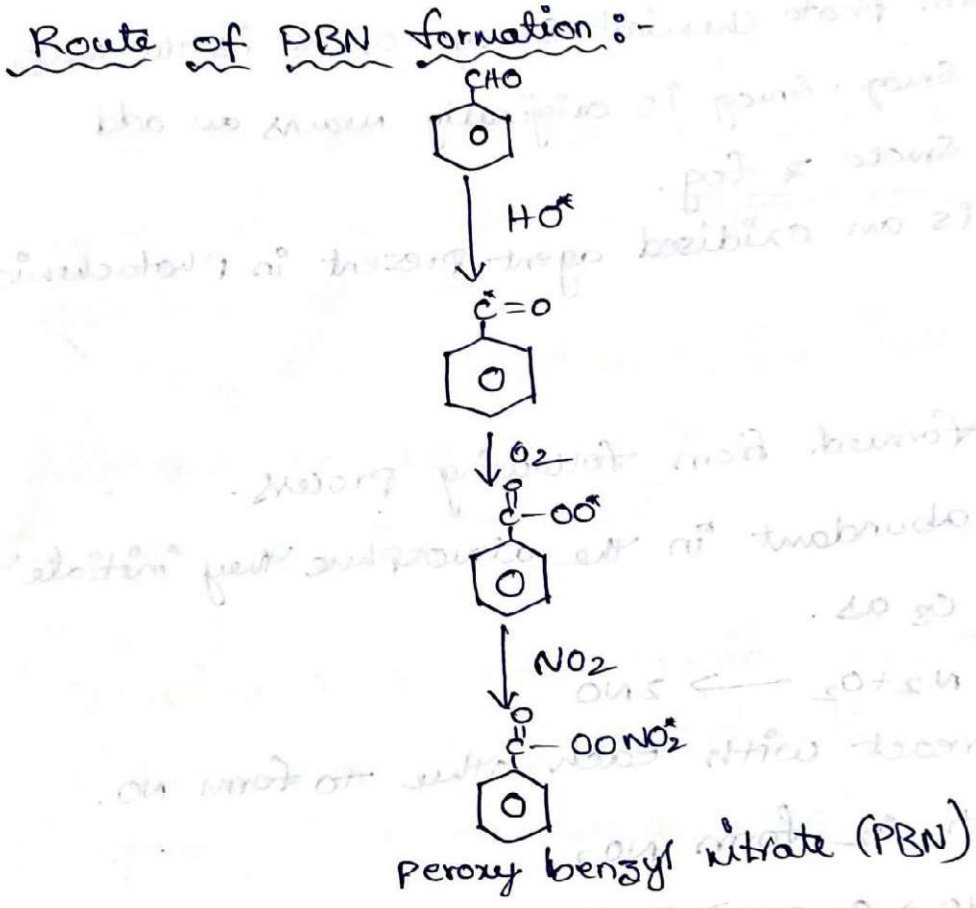
Both PANs and their chlorinated derivates are said to be mutagenic (Cancer causing agents) PANs are also cause the edema, i.e. accumulation of fluid in the lungs.

PANs behave has an oxidizing agent in solution & probably attack plants by oxidizing their -SH groups of proteins into disulphide.

This oxidation results in inhibition of individual enzyme activity.

Photo synthesis also affected by PAN. Enzymes in activated by PANs are isocitric dehydrogenate & 6-phaspate dehydrogenate.

2. Results of PBN formation:-


Route of PBN formation:-

Peroxy benzyl nitrate (PBN)

Controlling methods:-

PAN is secondary pollutants so their control ultimately depends on the control of their primary precursor, hydrocarbons and NOx.

3. Ozone (O_3):-

Source:-

Ozone is a secondary pollution, i.e., it is formed from primary pollutants, which reacts one another in presence of sunlight to form photochemical smog. Ozone is the major content is the smog. Smog is originally means an add combinations of smoke & fog. Ozone is an oxidized agent present in photochemical smog.

Formation:-

Ozone is formed from following process.

N_2 & O_2 are abundant in the atmosphere they initiate the formation of O_3 as

$$N_2+O_2 \rightarrow 2NO$$

N_2 & O_2 react with each other to form NO.

NO react with O_2 from NO_2.

$$2N+O_2\rightarrow 2NO_2$$

In the presence of sunlight NO_2 dissociates to form NO & O.

$$NO_2+h\nu\rightarrow NO+O$$

The formed oxygen is reacting with O_2 to form O_3 in presence of molecule (M).

$$O+O_2+M\rightarrow O_3+M$$

This is a molecule which absorbs the energy formed or emitted by the reaction. If it is not present O_3 dissociates back into O_2 & O by using energy O & O_2 reaction.

$$O_3+NO\rightarrow NO_2+O_2$$

The photochemical smog is formed in the presence of sunlight so increase in the sunlight the increase in the formation of O_3 and in cloudy days it's almost zero. The formation of O_3 is at weak in the now a time as the temperature is high.

The ozone formation is also initiated by the oxides of nitrogen .we should consider these only as O_3 from primary pollutants.

Effects:-

Increase in O_3 concentration near the earth surface reduces crop yields significantly.

Here the effects of human beings.

DNA damage:-

Focusing of UV-rays on skin leads to damage DNA.

Mutations in base pairs of DNAs causes of DNA damage (skin cancer, skin allergies), Future generation defects. Fruits of plants mainly damaged

E.g.: - Tobacco, Tomato, beans.

The rain fall failures on the earth. 1% reduction of O_3, 2% UV radiation on earth's destruction of aquatic life, Vegetation & loss of immunity, green house effect.

Control:-

Saving the 'ozone layer 'by British government & UNEP. The United Nations Environment Programmed (UNEP), established in 1972, addresses environmental issues at the global and regional level for the United Nations. The depletion of ozone layer is mainly due to CFCs (Controlled Foreign Companies Rules) the alternative to CFCs was designed by Japan companies. The device called 'ice cleaning' is a semiconductor washing device, which uses fine particles of ice & frozen alcohol at temperature below - 50^{o}c. Then result the low harmful effect compound in CFCs.

c) Standards for ambient air quality:-

Environmental protection agency in US set the national air quality standards only for primary pollutants called air quality standards for primary air pollutants.

Table -I

Air quality standards for planning air pollutants:-

S.NO	Pollutant	Tolerance (PPM)	Levels $\mu g/m^3$	Relative toxicity
1	CO	9.0 Not to be exhausted more than once/year for 8hr period.	10,000	1.0
2	COx	35.0 not are exhausted more than once/year for 1hr period.	40,000	-
3	Hydrocarbons	-	19,300	2.07
4	SO_x	0.56	1430	28.0
5	NO_x	0.25	514	77.8
6	Particulates	-	375	106.7

Table -II

Quality of pollutants collects per lit:-

S.NO	Pollutant source	Weight of pollutant produced						Total weight of pollution produce by each source
		CO	NOx	H_2S	SOx	Particulates		
						≤ 20μ	≥ 3μ	
1.	Transportation	69.7	10.1	10.0	0.8	1.2	1.0	93.6
2	Fuel combustion	1.2	11.8	1.4	21.9	4.6	1.3	42.2
3	Industrial process	7.8	0.7	9.4	4.1	6.3	2.7	31.0
4	Solid waste disposed	7.8	0.6	1.6	0.1	1.1	-	11.2
5	Miscellaneous	8.5	0.4	6.3	0.1	1.3	-	16.6
6	Total weight of each pollutant produced	95.0	23.6	29.5	27.0	19.5	-	194.6

UNIT-IV

KINETIC METHODS OF ANALYSIS AND NON AQUEOUS TITRIMETRY

a) Kinetic methods of analysis:-

Kinetic energy is a property of a moving object or particle and depends not only on its motion but also on its mass.

The kind of motion may be translation (or motion along a path from one place to another), rotation about an axis, the vibration or any combination of motions. The Kinetic energy is

$$E = mc_2.$$

The main characteristics of kinetic energy are movement and moving objects. Kinetic energy is never present in an object at rest only in objects that are moving.

Introduction:-

Chemical kinetics is the study of rate and mechanism of chemical reactions. The word of kinetic suggests that motion. Here kinetic refers to the rate of reaction (or) reaction rate.

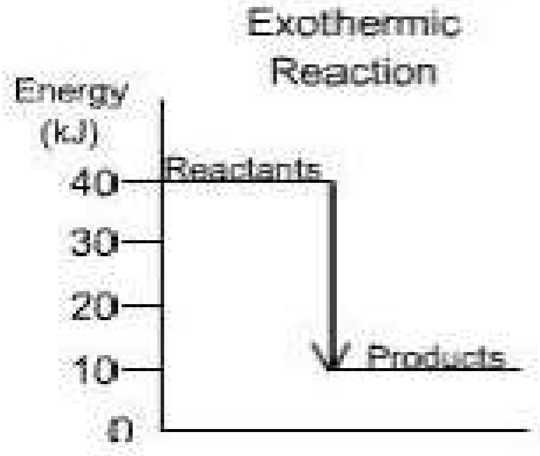
Rate of reaction (or) reaction rate:-

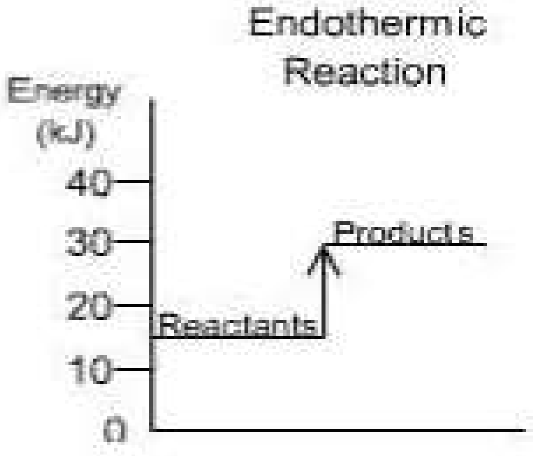
The rate of reaction is defined as the decreased conc. of reactants with the (or) the conc. of product increases with **c**onsiders a reaction.

$$A \rightarrow B$$

A→ Reactant

B→ Product





The rate of reaction with respective ‘A’ is given by,

$$\text{Rate} = -dc / dt \text{ (or) } -d[A] / dt$$

It is defined as decreases with the concentration of reactants.

Where,

Dc=is the small decreasing in conc. of ‘A’ in a small interval of time ‘dt’.

[A]= molar conc. of reactant ‘A’.

The negative sign indicates that concentration decreases with time. The rate is always positive quaintly.

Similarly, the rate of reaction with respect is to given by,

$$\text{Rate} = dx / dt \quad \text{or } d\,[B] / dt$$

Where,

dx (or) dt is the small increasing conc. of the product ‘B’ in a small interval of ’dt’.

[B] Molar conc. of product of ‘B’

The positive sign indicates that the conc. of ‘B’ increases that with the units of a reaction are $\text{mole.lit}^{-1}.\text{sec}^{-1}$

In gases the unity of the reactions are atm /sec. The reactions are **two types**.

1. Fast reactions:-

The rate of reactions depends up on the nature of reactants. The ionic substance in aqueous solution contains free ions. Ions can be direct participating reactions as bonds need to be broken. The ionic reactions are very fast. There are known as fast reactions.

Ex: - $AgNO_3 + KCL \rightarrow AgCl + KNO_3$

2. Slow reactions:-

Reaction between covalent substances is because in such reactions breaking of bonds & formation of new covalent bonds occurs.

The rusting of iron, the fermentation of sugar into alcohol, the chemical weathering of rocks(breaking down of rocks), the photo synthesis process in plants, coal formation are slow reactions.

Ex: -

Reaction b/w potassium permanganate and oxalic acid, Photo synthesis**,**

If many organic reactions are formed, these examples are digestion of fact rusting of iron.

The slow reaction possesses a low rate of reaction. They possess higher activation energy.

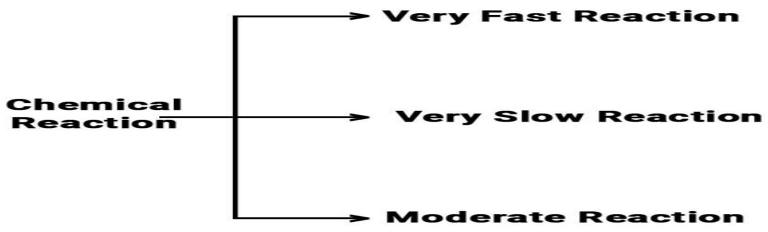
The example of slow reactions is rusting of a water pipe, a piece of newspaper turning yellow and so forth.

The fast reaction is defined as the reaction which takes a shorter time to complete.

Formation of crude oil by a geochemical reaction and disintegration of radium are other examples of slow reactions.

The chemical reactions complete in a very short time, such as less than 10^{-6} seconds, they are called fast reactions.

Similarly, a neutralization reaction between acids and bases is a fast reaction.



Depending upon the rate of reaction they are classified in three categories.

For example:-

Resting of iron (or) corrosion of iron:-

Rust is an iron oxide, a usually reddish-brown oxide formed by the reaction of iron and oxygen in the catalytic presence of water or air moisture. Rust consists of hydrous iron (III) oxides and iron (III) oxide- hydroxide, and is typically associated with the corrosion of refined iron.

Rusting is an oxidation reaction. The iron reacts with water and oxygen to form hydrated iron (III) oxide, which we see as rust. Iron and steel rust when they come into contact with water and oxygen – both are needed for rusting to occur.

The resting of iron is example of slow reaction. When iron is exposed to moist air, then a film of rust is found. The rust is hydrated in ferric oxide.

In metallic corrosion a metal is oxidized by loss of electrons generally to oxygen & results in the formation of oxides. Corrosion of iron (commonly known as rusting) occurs in present of H_2O & air.

At anode: - $Fe \rightarrow 2Fe^{+2}+4e^-$(Oxidation)

At cathode:-$O_2+4H^++4e^- \rightarrow 2H_2O$ (reduction)

Electrons are released at anodic spot move through the metal & go to another spot on the metal & reduce oxygen at in presence of H^+(hydrogen ion in water may also be available due to dissolution of other acidic oxides from the atmosphere). The spot behaves cathode with the reaction. The overall reaction is,

$$Fe+O_2+4H^+ \rightarrow 2H_2O+2Fe^{2+}$$

The ferrous ions are for then oxidized by atmospheric oxygen to ferric ions. Then comes out from rust in the form of hydrated ferric oxide and with for the production of hydrogen ions.

$$2Fe^{2+}+2H_2O+1/2O_2 \rightarrow Fe_2O_3+4H^+ \text{ (oxidation)}$$

Ex: - The reaction b/w hydrogen & oxygen at room temperature is a slow reaction.

Determination of slow reaction:-

These are determined by 2 methods.

1. Physical method

2. Density method

1. Physical method: -

Physical property can be followed through the (course) force reaction. Samples of reacting mixture can be taken at suitable intervals and they are analyzed by measuring some physical properties. Which are conveniently done time to the reacting substance without disturbing the rate of reaction.

2. Density method:-

The density technique involves the measurement of change in the volume. This change in volume can be measured by dilatometer. This dilatometer consists of bulb provides with a side tube through which can be filled with an opened capacity. After then bulb is filled with reacting mixture, the suitable is using closed cork.

The partition of the meniscus of the capacity can be directly read from the scale. This type of technique can be applicant the most of reactions takes place in liquid. This is especially used for slow reactions and moderately rapid reactions.

Catalyzed reactions:-

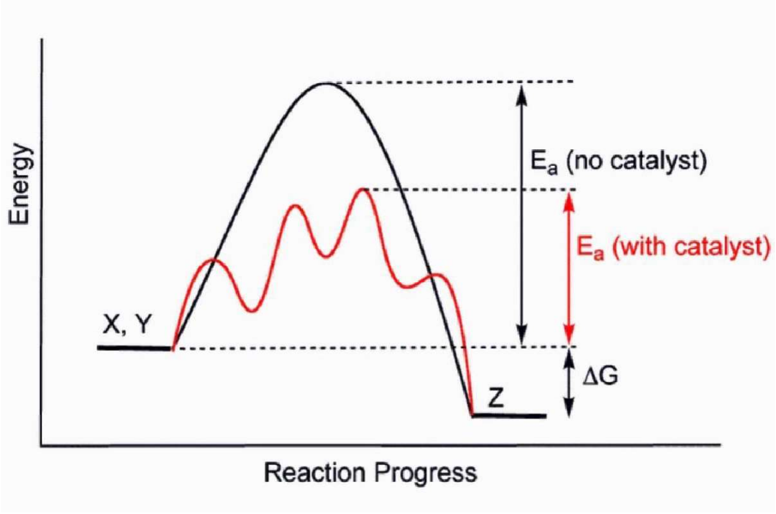
Catalyst:-

Catalyst is defined as the increasing the rate of a chemical reaction by introducing a catalyst.

A catalyst is a substance that is not consumed by the chemical reaction, but acts as to lower its activation energy.

In other words, a catalyst is both a reactant and product of a chemical reaction.

A very small quantity of catalyst is required in order to the catalyze reactions.



Types of catalyst reactions:-

Catalysts are primarily categorized into four types. They are,

(1) Homogeneous

(2) Heterogeneous (solid),

(3) Heterogenized homogeneous catalyst and

(4) Biocatalysts.

Mainly catalysts can be classified into two types: -

Homogeneous and Heterogeneous:-

Homogeneous catalysts are those which exist in the same phase (gas or liquid) as the reactants, while heterogeneous catalysts are not in the same phase as the reactants.

Characteristics of Catalysts:-

The catalyst remains unchanged (in mass & chemical composition) in the reaction (Activity of catalyst.)A small quantity of the catalyst is required. The catalyst does not change the equilibrium constant. The catalyst cannot make impossible reaction to occur and does not initiate a reaction.

Applications of catalysis:-

Industrial applications:-

Almost all chemical industries have one or more steps employing catalyst. **Ex: -** petroleum, energy sector, fertilizer, pharmaceutical, fine chemicals.

Environmental applications:-

Pollution controls in combination with industrial processes. Pre treatment- reduce the amount waste/change the composition of emissions Post- treatments- once formed reduce and convert emissions The using is alternative materials.

Catalyzed reactions:-

Enzymes are high molecular weight protein molecules that catalyzed reactions of importance in biology & biomedicine.

Ex: - Consider a reaction b/w Ce (IV) & As (III)

There is some disagreement about the extract mechanism .all though caller research had indicated 3rd order kinetic. The work of established the existence of As (IV) as on intermediate the two steps mechanism.

$$\text{Ce (IV)} + \text{As (III)} \rightarrow \text{Ce (III)} + \text{As (IV)}$$

$$\text{Ce (IV)} + \text{As (III)} \rightarrow \text{Ce (III)} + \text{As (V)}$$

The intermediate species is a strong reducing agent. In the presence of iodide (or) iodine a pronounced analysis occurs properly the following equation.

$$\text{Ce (IV)} + I^- \rightarrow I^0 + \text{Ce (III)} = (2I^0 \rightarrow I_2)$$

$$I_2 + H_2O \rightarrow HOI + H^+ + I^-$$

$$H_3AsO_3 + HOI \rightarrow H_3AsO_4 + H^+ + I^-$$

Because of all the reactions is involving iodine (or) rapid. Sandal and other described determination of ruthenium (Ru) & osmium (Os) based on catalysis of the Ce (IV) & As (III) reactions. In both cases the reactions rate is proportional to catalyst concentration.

However with ruthenium the rate is independent of As (III) dependent on Ce (IV) where as with osmium the rate is dependent of Ce (IV) & dependent on AS (III).

$$As(III) + Os(VIII) \rightarrow As(V) + Os(VI)$$

Another example of homogeneous catalysis is that H_2O_2 acts as both an oxidant and a reductant with two different reactions proceeding in characteristics rates under a given set of conditions.

$$H_2O_2 + 2HBr + 2H^+ \rightarrow Br_2 + 2H_2O$$

$$H_2O_2 + Br_2 \rightarrow O_2 + 2H^+ + 2Br^-$$

Methods of determination of catalyst concentration:-

Enzymatic reactions are examples of catalysis reactions. They can be formatted in a generalized way. E & S are enzyme & subtract, enzyme react with subtract to produce enzyme subtract complex.

$$E + S \leftrightarrow [ES]\ (K_1, K_2)$$

$$[ES] \rightarrow P\ (K_3)$$

Here 'P' is the product & 'ES' is the addition complex. They steady statement was first applied to the mechanisms.

$$RATE = d[ES]/dt$$

$$= K_1 [E] [S] - K_2 [ES] - K_3 [ES] = 0$$

$$= K_1 [E] [S] - [K_2 + K_3] [ES] = 0 \rightarrow \textbf{Eq-1}$$

In studies enzyme reactions the molar conc. of subtract is usually very much greater than that of enzyme only. A small portion of subtract therefore is bound to the enzyme the total conc. of $[E]_0$ is equal to the conc. of free enzyme [E] is & the conc. of the complex [ES].

$$[E]_0 = [E] + [ES]$$

$$[E] = [E]_0 - [ES] \rightarrow \textbf{Eq-2}$$

Eq-2 is substitute in **Eq-1**

$$= K_1 [[E]_0 - [ES]] [S] - (K_2 + K_3) [ES] = 0$$

$$= K_1 [E]_0 [S] - K_1 [ES] [S] - (K_2 + K_3) [ES] = 0$$

$$= K_1 [E]_0 [S] - [ES] [K_1 (S) + (K_2 + K_3)] = 0$$

$$= K_1 [E]\ 0\ [S] = [ES] [K_1 (S) + (K_2 + K_3)]$$

$$[ES] = K_1 [E]_0 [S] / K_1 (S) + (K_2 + K_3)$$

$$[ES] = K_1 [E]_0 [S] / K_1 [[S] + [K_2 + K_3] / K_1)]$$

$$[ES] = ([E]_0 [S] / [S] + [(K_2 + K_3) / K_1)]$$

$$[ES] = ([E]_0 [S] / [S] + K_m$$

$$\therefore (Km = K_2 + K_3 / K_1)$$

∴ Km=Michael son Manton constant

Case-1:-

Conc. of substrate [S] is sufficiently small it may be neglected in the denominator by compare with Km.

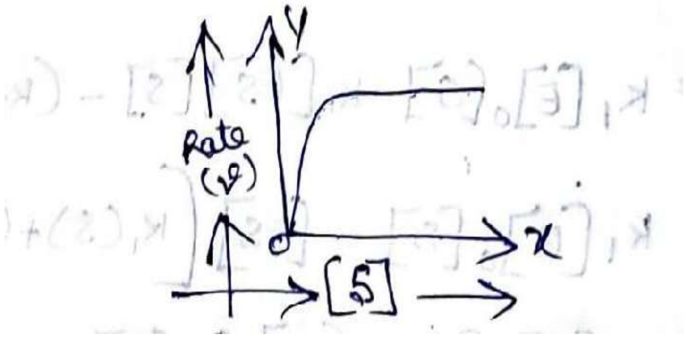
i.e., $[S] <<<<< Km$

$[ES] = [E]_0 [S] / Km$

$Rate = K_3 [ES]$

$Rate = K_3 / Km [E]_0 [S]$

So, that the kinetics is first order the graph is drawn b/w conc. of student & rate varies linearly.



Case-2:-

Conc. of subtract [s] is greater than the km, i.e.

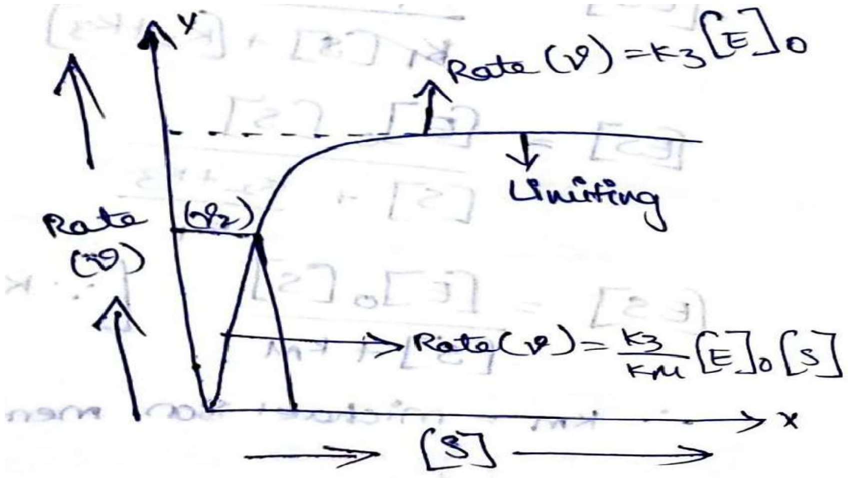
$[S] >>>> Km$

$[ES] = [E]_0 [S] / [S]$

$[ES] = [E]_0$

$Rate = K_3 [ES]$

$Rate = K_3 [E]_0$



Extrapolation method for the determination of catalyst:-

Extrapolation:-

Extrapolate means to insert points either before the first known point, or, after the last known point on the graph.

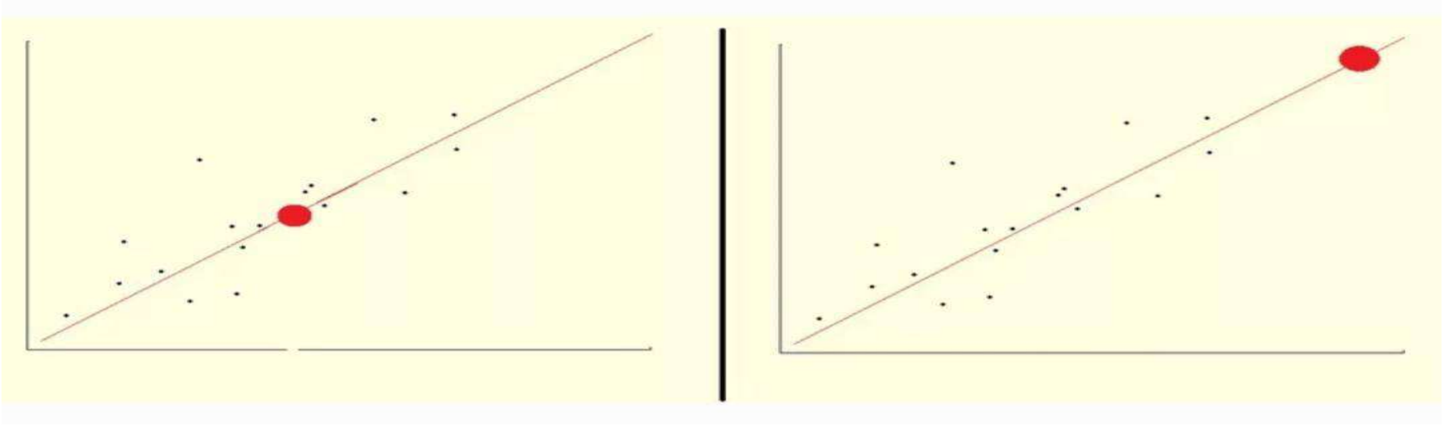
The estimate of the value of a result in outside the range of a series is known values. Technique used in standard additions calibration procedure.

Interpolation:-

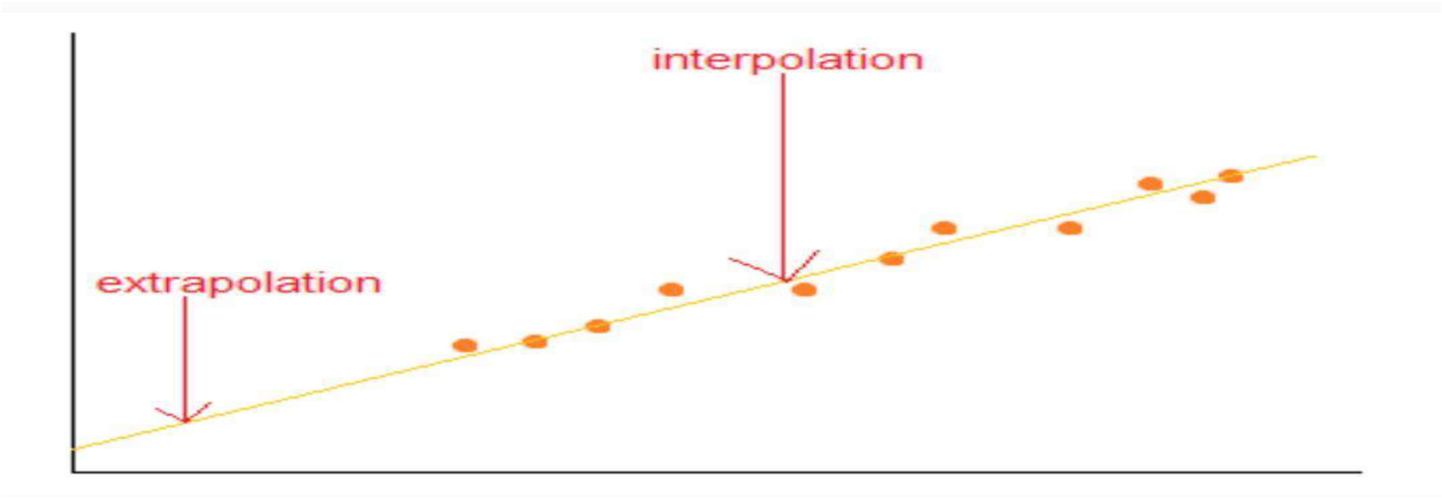
Interpolation is the process of using known data values to estimate unknown data values. Various interpolation techniques are often used in the atmospheric sciences.

One of the simplest methods, linear interpolation, requires knowledge of two points and the constant rate of change between them.

Extrapolation is an estimation of a value based on extending a known sequence of values or facts beyond the area that is certainly known. Interpolation is an estimation of a value within two known values in a sequence of values. Polynomial interpolation is a method of estimating values between known data points.



Predicting within the range of data is called interpolation. In the case where predictions are made outside of the data range, then those predictions are called extrapolations.



Variable time integral method:-

In variable time integral method we measure the time required for a reaction proceeds by a find amount. Here initial conc. of the analyte is determined by elapsed time (Δt). The imp application of this method is quantitative analysis of this analyst which is based on the ability of the catalyst to increases the rate of reaction. As the initial conc. of the catalyst increases the time required to reach the reaction decreases. The relationship b/w initial conc. of catalyst & elapsed time is

$$1 / \Delta t = [A]_0 [F_{catalyst} + F_{uncatalyst}]$$

Where,

$[F_{catalyst} + F_{uncatalyst}]$ are constant which the functions are of rate constant for catalyzed & unanalyzed reactions during the time [t] & Δt.

Fixed time integral method:-

Integral method for analyzing kinetic data makes use of the integral form of rate law. In one point fixed time (result) integral method the conc. of analyte is detected at single time initial conc. of analyte 'A_O' is calculated following.

The reaction is first order (or) pseudo first order reaction. The reaction concentration for the reaction is separated experiment used in standard solution of analyst. Suppose the reaction follows pseudo 1st order reaction. The rate is given by,

$$[A]_t = [A]_0 e^{-kt} \rightarrow \textbf{eq-1}$$

$$\ln [A]_t = \ln [A]_0^{-kt}$$

$$Kt = \ln [A]_0 - \ln [A]_t$$

$$Kt = \ln [A]o / [A]_t$$

$$Kt = 1/ t (\ln [A]_O / [A]_t)$$

$$K = 2.303 / t (\log [A]_o / [A]_t)$$

Sometimes, it is more convenient to monitor the progress of the reaction with respective the conc. of the analyte & products in the reaction.

$$A+R \rightarrow P$$

$$[A]t = [A]_0 - [P] t \rightarrow \textbf{eq-2}$$

$$[A]_0 e^{-kt} = [A]_0 - [P] t$$

$$[P]t = [A]_0 - [A]_0 e^{-kt}$$

$$[P]t = [A]_0 (1- e^{-kt})$$

$$[A]_0 = [P]t / (1- e^{-kt})$$

From this equation we can calculate the initial conc. of the analyte.

Where 'R' is a reagent which is used in excess so the reaction proceeds pseudo first order reaction the concentration of analyte at time 't' is given by,

For a fixed time integral method in which the conc. of analyte for pseudo first order reaction the measured at At_1 and At_2 we can write,

$$[A]t_1 = [A]_0 e^{-Kt_1} \rightarrow \text{eq-3}$$

$$[A]t_2 = [A]_0 e^{-kt_2} \rightarrow \text{eq-4}$$

$$\text{Eq3 - Eq4}$$

$$[A]t_1 - [A]t_2 = [A]_0 (e^{-kt_1} - e^{-kt_2})$$

$$[A]_0 = [A]t_1 - [A]t_2 / e^{-kt_1} - e^{-kt_2}$$

Examples for the determination of toxic metals and anions by using some typical kinetic reactions:-

Determination of toxic metals:-

In this many inorganic anions and cations are catalysis inorganic reactions. The reactions those rates are measured by such as spectro photo metrically.

The rate of reaction is directly proportional to the concentration of catalyst. Then data is concentration can be defined.

Example of this method involves the kinetic determination of Hg^{+2} catalytic effects on hexa cyano ferrous (II) with nitraso benzene as been employed to determine Hg^{+2}.

The uncatalyzed indicator proceeds to

$$[Fe(CN)_6]^{-4} + H_2O \rightarrow [Fe(CN)_6H_2O]^{-3} \rightarrow \textbf{Eq1} \text{ (slow)}$$

$$[Fe(CN)_5H_2O]^{-3} + C_6H_5NO \rightarrow [Fe(CN)\ 5C_6H_5NO]^{3-} \rightarrow \textbf{Eq2} \text{ (fast)}$$

In the presence of Hg+2 accelerates in the second step by mainly cyanide from the intermediate compound $[Hg\,CN]^+$. The react with H^+ present in the solution by liberating the Hg^{+2} ions.

$$Hg^{+2} + CN^- \rightarrow [Hg\,CN]^+$$

$$[Hg\,CN]^+ + H^+ \rightarrow Hg^{+2} + HCN$$

In eq2 is very fast & serve as integrated reaction for monitory. In which the formation of product spectro photo metrically at 525 nm. The formation of the product is consistent with the general catalyst mechanism.

The rate of reaction is given by following.

$$\text{Rate} = d / dt\, [Fe(CN)_5C_6H_5NO]^{3-}$$

Here,

K catalyst, [Hg] catalyst

Rate formation of product is directly proportional to conc. of catalyst by fixed time integral method at time = 8000secs.

Hg^{+2} determine by the level as 3×10^{-7} molar.

This type of method can be used for determine of Hg^{+2} on biological material & industrial products.

b) Non-aqueous titrations:-

It is a type of titration in which the analyte substance is dissolved in a solvent that does not contain water.

Difference between aqueous and non-aqueous titration:-

The solvents are used in aqueous contain water, where as in non - aqueous, the solvent does not contain water.

The non-aqueous titration is based on which theory is Brownsted –Lowry theory. According to this theory, an acid is a substance which will tend to donate a proton and a base is any substance, which will accept a proton.

Common examples are liquid ammonia, liquid sulfur dioxide, sulfuric chloride & sulfuric chloride fluoride, phosphoric chloride, di nitrogen peroxide, antimony dichloride, bromine pent fluoride, hydrogen fluoride, pure sulfuric acid and other inorganic acids.

It is used for determination of concentration expressions. It is used in determination of hydrophobic compounds, phenobarbitone, diuretics, and steroids. It is used in the determination of composition of ant tubercular drugs.

Classification of solvents:-

According to Brownsted-Lowry theory non-aqueous solvents are classified into four types. There are,

1. Protophilic solvents

2. Protogenic solvents

3. Amphoteric solvents or Amphiprotic solvents

4. Aprotic solvents.

1. Protophilic solvents:-

The substance which great tendency to accept protons from another substance is called protophilic solvents.

Ex: - H_2O, NH_3, R-OH

2. Protogenic solvents:-

The substance which grate tendency to donate (or) generate protons from another substance is called photogenic solvents.

Ex: - H_2O, HCL, glacial acetic acid.

3. Amphoteric solvents or Amphiprotic solvents:-

The substance which great tendency to accept protons as well as to donate protons from another substance is called amphoteric solvents.

Ex: - H_2O, HCO_3^-, NH_3, HSO_4^-, H_2SO4^-, R-CH

4. Aprotic solvents:-

The substances which do not donate (or) accept proton is called aprotic solvents.

Ex: - Benzene, carbon tetrachloride (CCl_4).

Solvents for non-aqueous titrations:-

A very large no of both inorganic & organic solvents have been used for non-aqueous determinations. There are,

1. Glacial acetic acid

2. Acetonitrile (or) methyl cyanide

3. Alcohols

4. Dioxime

5. Dimethyl formamide

1. Glacial acetic acid: -

It is most frequently employed solvent .The water content in glacial acetic acid may be lies b/w 0.1-1% and add just sufficient acetic anhydride to water convert a glacial acetic acid.

$$C_4H_6O_3 + H_2O \rightarrow 2CH_3COOH$$

2. Acetonitrile (or) methyl cyanide:-

It is frequently used with other solvents such as $CHCl_3$, phenol & CH_3COOH. It gives very sharp and point to be obtained in the filtration of metal acetates when titrations perchloric acid.

3. Alcohols:-

This is most used for the determination of salts of organic acids. They most combination is ethylene glycol with Propane - 2- ol (or) butane-1-ol. The combination provides the solvents power for the both polar & non polar of the molecule.

4. Dioxime:-

It is another popular solvent, which is used in place of glacial acetic acid unlike acetic acid. It gives the separate end points corresponding to the individual components in the mixture.

5. Dimethyl formamide:-

It is a protophilic solvent, which is frequently employed for titrations b/w benzoic acids and amides.

Indicators for non-aqueous titrations: -

The majority of non- aqueous titrations are carried out by using a fairly limited range of indicators. The indicators are,

1. Crystal violet

2. Methyl red

3. 1-Naphthol benzene

4. Quanalidine red

5. Thymol blue

6. Oracel blue ‘B’

1. Crystal violet: -

It is used as 0.5 %(w/v) solution in glacial acetic acid. Its color change from violet to blue & followed by green to greenish yellow observed in the bases reactions of pyridine titrated with perchloric acid.

2. Methyl red:-

It is used as 0.2% solution in dioxime. The color changes are yellow to red color.

3. 1-napthol benzene: -

It is used as 0.2% solution in an acetic acid .Its gives color change from yellow – green. It gives sharp end points in nitro base against perchloric acids.

4. Quanalidine red:-

It is used as 0.1 %(w/v) solution in ethanol. It gives a color change from purple red to pale green It is used as the indicator for drug determination is dimethyl formamide solution.

5. Thymol blue: -

It is used as 0.2 %(w/v) solution in methanol. It gives a color change from yellow to blue .It is extensively used as the indicator for titrations of substances acting as acids in dimethyl formamide solution.

6. Oracel blue ‘B’: -

It is used to as 0.5 %(w/v) solution in CH_3COOH & is consider being superior to crystal violet for titrations of bases in acetic acid with standard perchloric acid. The end point is change from blue to pink.

Acid & Base:-

An acid is a substance that donates protons (in the Brownsted-Lowry definition) or accepts a pair of valence electrons to form a bond (in the Lewis definition). A base is a substance that can accept protons or donate a pair of valence electrons to form a bond.

Acids have a pH less than 7. Alkalis have a pH greater than 7 Neutral substances have a pH equal to 7. Acids contain lots of hydrogen ions, which have the symbol H^+. Alkalis contain lots of hydroxide ions, symbol OH^-.

Difference between Acids and Bases:-

Acids:-

Acid gives off hydrogen ions when dissolved in water. It turns blue colour litmus paper into red. It has a sour taste.

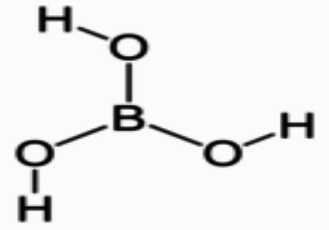
Bases:-

Bases give off hydroxyl ion when dissolved in water. It turns red colour litmus paper into blue. It has bitter taste and soapy to touch.

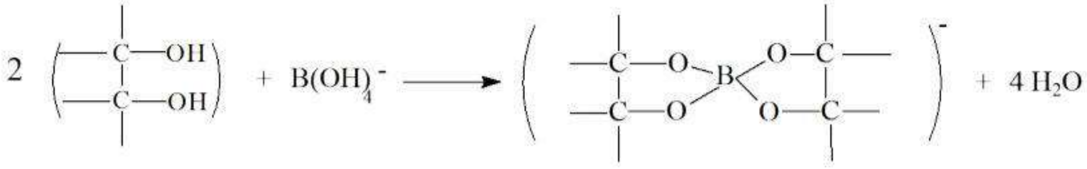
i) Determination of acids:-

1. Determination of boric acid: -

Structure:-



Boric acid is acts as a weak mono protic & hence it can’t be titrated accurately with standard alkali. The addition of certain organic poly hydroxy components such as mannitol, glucose, glycerol. Its acts as a much stronger acid are used with a phenolphthalein as an indicator.



Commercially the boric acid may contain ammonium salts. It is necessary to act and slight excess of Na_2CO_3 solution then boil the solution to expel the ammonia & filter the solution in case of turbidity is formed. The filtrate is neutralized with methyl red. After then boiling & then to this add a mannitol. The resulting solution is titrated with NaOH solution.

Procedure:-

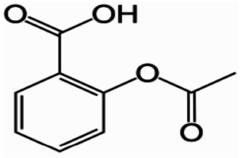
Weighed out accurately 0.5g of boric acid is taken into a 250ml volumetric flask and make up to the mark with distilled water. After then pipette out 25 ml of above solution is taken into a conical flask & then equal amount of water & 2 or 3 grams of mannitol or sarbitol. After then this solution is titrated with 0.1 M NaOH solution by using phenolphthalein as an indicator.

$$H^+ \text{ (boric acid complex)} + NaOH \rightarrow Na \text{ (boric acid complex)} + H_2O$$

Factor: - 1ml of 0.1 M NaOH = 0.06184g of H_3BO_3

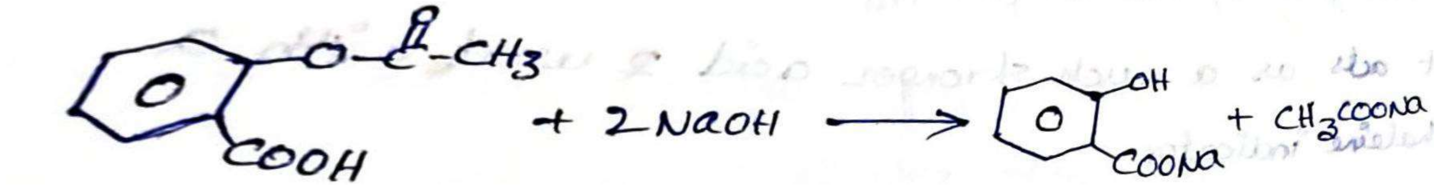
2. Aspirin (Acetyl salicylic acid):-

Structure:-



Principle: -

The aspirin under goes hydrolysis, then it is treated with a warm solution of NaOH, then to producing sodium acetate (CH_3COONa) & sodium salicylate. In this used to the excess of NaOH. After then untreated NaOH is may be determined by back filtration with standard HCL solution.



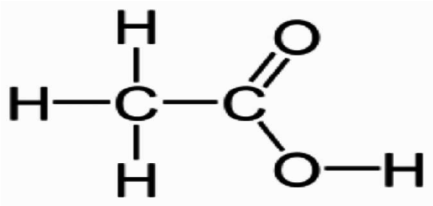
Procedure:-

Accurately weighed 1.2g of acetyl salicylic acid & transfer into 250mL volumetric flask, then to this added 50 ml of 0.5M NaOH solution & heat the resulting solution on water both for 10min. allow the solution to cool & excess amount of NaOH is back titrated with standard HCL solution by using 3 drops of quanalidine as an indicator.

Factor:-1ml of 0.5M NaOH=0.0450g of Aspirin

3. Determination of glacial acetic acid:-

Structure:-



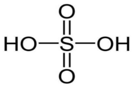
Accurately weighed 2g of glacial acetic acid is taken into a conical flask. After then to this added 20mL graduated flask. Then flask is washed with water with several times and then to this added distilled water & it is boil, after then to take 25mL of acid solution is taken from the above solution. Finally then it is titrated with 0.1M NaOH solution.

$$CH_3COOH+NaOH \rightarrow CH_3COONa+H_2O$$

Factor: - 1mL of 0.1M NaOH = 0.06005g of CH_3COOH

4. Determination of H_2SO_4:-

Structure:-



Place above 100mL of water in a 250ml of graduated flask. After then to this added 1.32 - 1.45g of H_2SO_4 solution. The flask stand for one (or) two hours to regain the laboratory temperature & then shakes & mix thoroughly & then titrated with 25mL of Acid solution titrated with standard 0.1M NaOH solution.

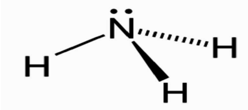
Factor:-1mL of 0.1M NaOH = 0.4904g of H_2SO_4.

ii) Determination of bases:-

1. Determination of Ammonia in ammonium salts:-

These are determined by 2 methods.

Structure:-



a) Direct method:-

In this method a solution of ammonium salt is treated with a solution of strong base & the mixture is distilled. Ammonia is quantitatively expelled & it is observed in an excess of standard acid. The excess of untreated acid is back titrated with standard NaOH the presence of methyl red or methyl orange indicator.

$$NH_4^+ + OH^- \rightarrow NH_3\uparrow + H_2O$$

Procedure:-

For this experiment, we used in the kejedhal flask, After then accurately weighed out 1.5g of NH_4Cl, it is dissolved in water, Then make up to the 250mL volumetric flask & mark with distilled water. Then this solution is shaking thoroughly & transfer into 50mL of the solution is taken into a distillation flask & dilution with 200mL of water. Then transfer into 100mL of 10% NaOH solution in the funnel (burette) run the NaOHs solution into the flask. Heat the distillation flask for 30-40 min by which all the ammonia should be passed over into receiver flask. Now few drops of methyl red indicator are added & the excess of acid in the solution with standard 0.1M NaOH solution.

Factor: - 1mL of 0.1M HCL=1.701g of ammonia

b) Indirect method:-

The ammonia salt is boiling with a known excess standard NaOH solution. Then boiling is continued until no more ammonia expel with the stream. The excess of NaOH is titrated with against the standard acid by using methyl red as indicator.

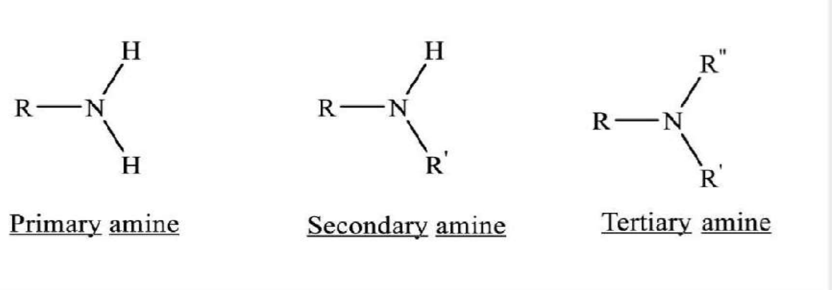
Procedure: -

Accurately weighed out 0.1 - 0.2g of the ammonia salt is taken into a 500mL of conical flask & then to this added 100mL of standard 0.1M NaOH solution & boils the mixture, until ammonia is completely expelled and cools the solution. After then to this added a few drops of methyl red as an indicator & titrated with 0.1M HCl solution.

2. Determination of amines:-

The purity of the adrenaline sample can be determined by the titrating with standard perchloric.

Structure:-



Preparation of perchloric acid:-

Prepare exactly 0.1M perchloric acid solution by adding slowly 2.1mL of 72% of perchloric acid to 100mL of glacial acetic acid & then to this added 50mL of acetic anhydride. Cool the solution & make up to 250mL with the acetic acid.

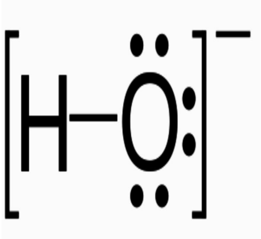
Procedure: -

Accurately weighed 0.4g of amine sample is taken & transfer into 250mL volumetric flask. Then dissolve amine in 70mL of glacial acetic acid & then added water to the solution, After then cool the resultant solution & titrate with 0.1M per chloric acid in the presence of acetic acid by using crystal violet is used as indicator .

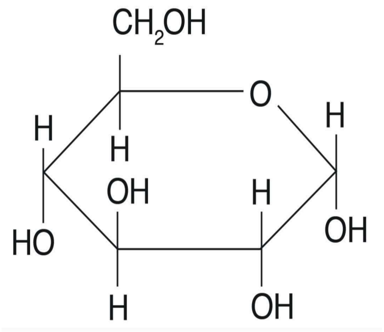
Factor: - 1mL of 0.1M $HClO_4$ = 0.083g of Adrenaline.

3. Determination of hydroxyl groups in carbohydrates:-

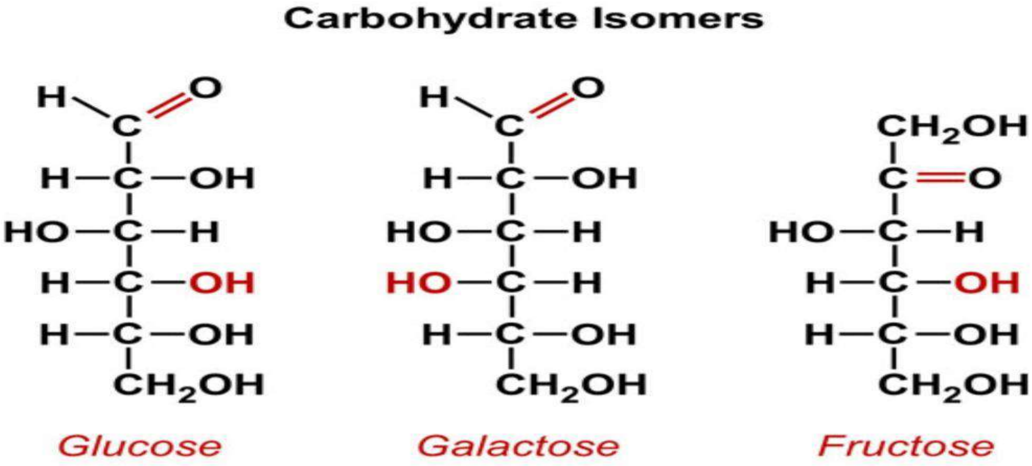
Structure of hydroxyl group:-



Structure of carbohydrates:-



Carbohydrates in term forms:-



Principle:-

Hydroxyl groups present in carbohydrates can be ready estimated by ethyl acetate containing some $HClO_4$. This reaction is used for determination of no. of hydroxy group in carbohydrate molecules is carried out the reaction with excess of acetic anhydride. The untreated acetic a hydride is back titrated with standard NaOH solution.

Chemicals required: - Acetic anhydride, NaOH, Perchloric acid.

Procedure:-

Accurately weighed 0.2g of carbohydrate is taken into a 100mL volumetric flask & dissolves water & then make up to the mark with distilled water. Above the solution is to take 10mL solution is taken into a conical flask. Pipette out 5mL of acetic anhydride/ethyl acetate solution is added. Carefully mix the contents until the solid dissolves, then add 10mL of pyridine water & allow the mixture, then to stand for 5 min, then treated with excess amount of acetic anhydride. Then untreated acetic a hydride is the titrated with standard NaOH solution with indicator.

No. of moles of hydroxyl groups in carbohydrates = Vb – Vs / 2000

Vb = Volume of NaOH consumed by blank solution.

Vs = Volume of NaOH consumed by sample solution.

iii) Karl-Fischer reagent for the determination of moisture content in drugs and other samples:-

In this technique is used for the determination of small amount of water in verify of organic & in organic solid and liquid samples. Karl Fischer was a German chemist. In 1935 he published a method to determine trace amounts of water in samples. This method is now called Karl Fischer titration.

What Is Karl Fischer Titration?

Karl Fischer titration is a titration method that uses volumetric or caloric metric titration to determine the quantity of water present in a given analyte. This method for quantitative chemical analysis was developed by the German chemist Karl Fischer in the year 1935, Today, specialized titrations (known as Karl Fischer titrations) are available to carry out such titrations.

Principle of Karl Fischer Titration:-

In this 3 steps are involved in the determination of water by Karl- Fisher techniques.

Step-1:-

The principle of Karl Fischer titration is based on the oxidation reaction between iodine and sulphur dioxide.

Water reacts with iodine and sulphur dioxide to form sulphur trioxide and hydrogen iodide. An endpoint is reached when all the water is consumed. The chemical equation for the reaction between sulphur dioxide, iodine, and water (which is employed during Karl Fischer titration) is provided below.

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

Step-2:-

In the second stage SO_3 forms a complex with pyridine.

$$C_5H_5N + SO_3 \rightarrow C_5H_5NSO_3$$

Step-3:-

This third stage is involves reaction of pyridine complex with methanol to form stable complex.

$$C_5H_5NSO_3 + CH_3OH \rightarrow C_5H_5NHOCH_3OSO_2$$

The overall reaction is,

$$SO_2^{+} + I_2 + CH_3OH + H_2O + 3C_5H_5N \rightarrow 2C_5H_5NH^{+}I^{-} + OSO_2OCH_3\text{-}C_5H_5H\text{-}H$$

How can the KF reagent be prepared:-

Make a solution by mixing 170mL of pyridine and 670mL of methanol. Add 125g of iodine to the solution and cool it. Take a 250mL graduated cylinder and add 100mL of pyridine. Keep it on an ice bath. Pass in sulphur dioxide (dry) till its volume reaches 200mL.

Karl Fischer Titration Procedure:-

The Karl Fischer titration experiment can be performed in two different methods. **They are:-**

1. Colorimetric determination – The endpoint is detected in this experiment electrochemically. Iodine required for KF reaction is obtained by anodic oxidation of iodide from solution.

2. Volumetric determination – This technique is suitable to determine water content down to 1% of water. The sample is dissolved in KF methanol and the iodine is added to KF Reagent. The endpoint is detected potentio metrically.

1. Colorimetric titration:-

The sample is added to an electrolytic solution, the main constituents of which are iodide ions, sulfur dioxide, a base, and a solvent (such as alcohol). Electrolytic oxidation causes the production of iodine, resulting in an immediate Karl Fischer reaction.

$$2I'' - 2e \Rightarrow I_2$$

According to Faraday's laws, the iodine is produced in proportion to the quantity of electricity. This means that the water content can be determined immediately from the coulombs required for electrolytic oxidation.

1mg of water = 10.71 Coulombs

As shown in Figure, two types of colorimetric reagents are required: an analyte, which is placed in the anode chamber of the electrolysis cell, and a catholyte, which is placed in the cathode chamber. Colorimetric reagents do not need assessment. Another advantage is that they can be used repeatedly.

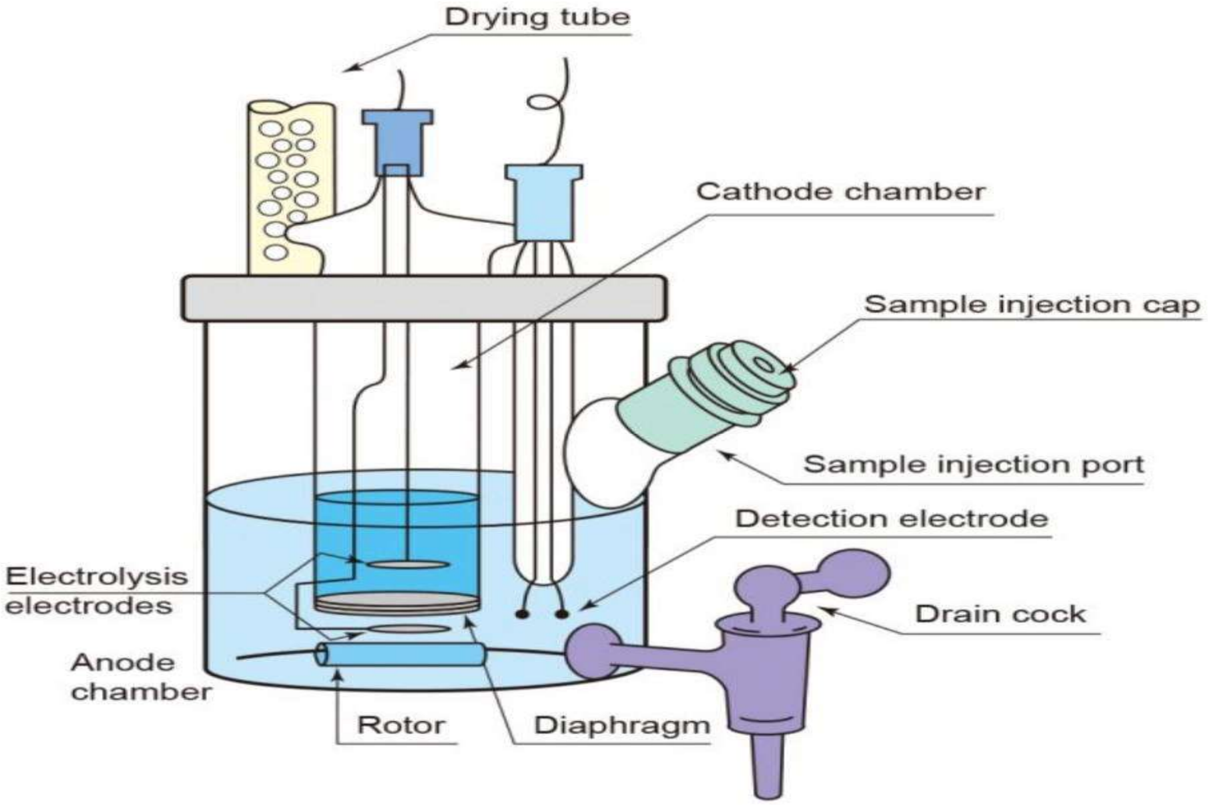


Figure1: Electrolysis cell of Coulometric Moisture Meter

2. Volumetric Titration:-

A dehydrating solvent suitable for the sample is placed in a flask. Titrant is used to remove all moisture from the solvent. The sample is then added. Titration is carried out using a titrant, the titer (mgH_2O/mL) of which has previously been determined. The moisture content of the sample is determined from the titration volume (mL). The end point is detected using the constant-current polarization voltage method. The figure shows the components of typical commercially available automatic volumetric titration system.

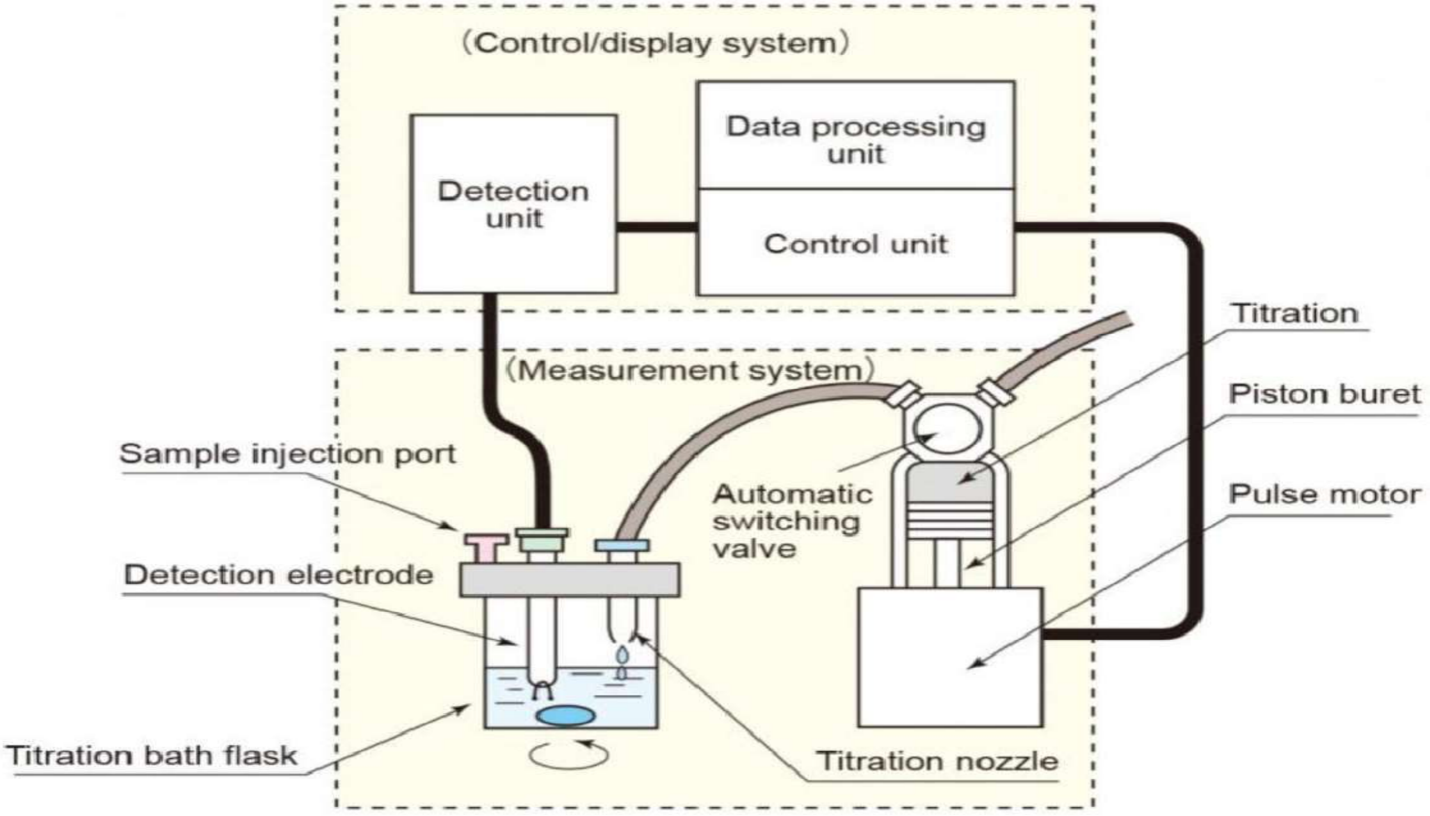


Figure2: Volumetric Moisture Meter

Examples:-

1. Oxidising agents:-

Such as chromates, dichromate's, Cu^{+2}, Fe (III) salts, higher oxides & peroxides.

$$MnO_2+2C_5H_5NH^+I^- \rightarrow Mn^{+2}+C_5H_5N+I_2+H_2O$$

2. Reducing agents:-

Such as thio sulphates into Tin (II) salts, sulphide compounds. It can be regarded as forming water with the components of KF reagents.

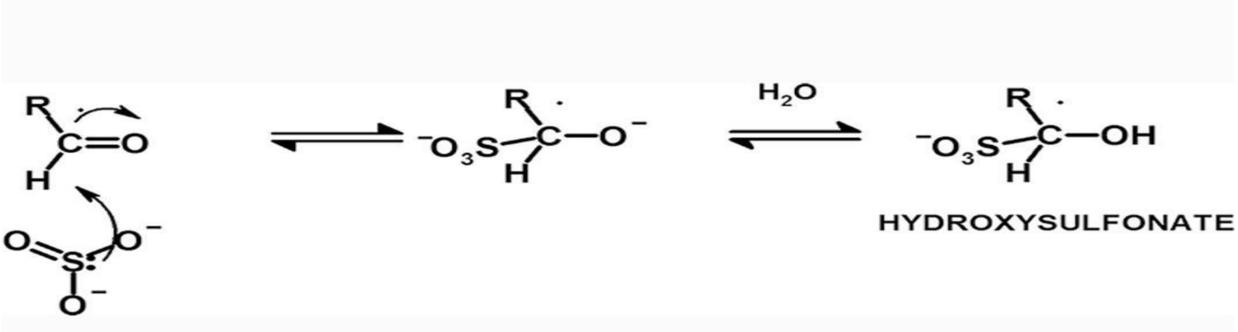
3. Basic oxides:-

$$ZnO+2C_5H_5NH^+ \rightarrow Zn^{+2}+C_5H_5N+H_2O$$

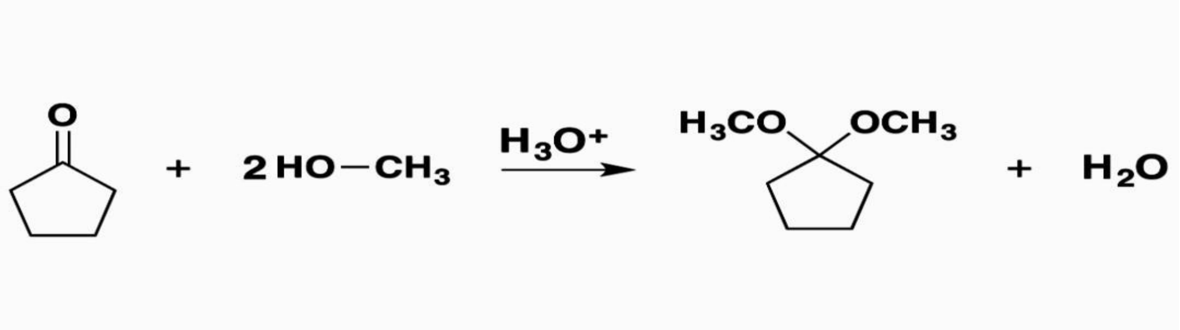
4. Salts of weak oxyacides:-

$$NaHCO_3 + C5H_5NH^+ \rightarrow Na^+ + H_2O + CO_2 + C_5H_5N$$

5. Aldehydes form a bisulphate product.



6. Ketones react with methanol to produce Katol & water.



Difference between volumetric method & colorimetric method:-

Colorimetric method – the titrant is produced electrochemically inside the titration cell.

Volumetric method – the titrant is directly added to the sample with the help of a burette.

Limitations of Karl Fischer Titrations:-

It is a destructive technique.

The solvent consumption is high as the manual volumetric titration demands reloading during each determination.

Colorimetric titration is fitted only for samples that contain a small amount of water.

Colorimetric titration takes extremely long periods to determine.

Karl Fischer Titration Applications:-

It is used in technical products such as plastics, oils, gases.

It is used in pharmaceutical products.

It is used in cosmetic products.

It is used in the industry

Advantages of Karl Fischer Titrations:-

It is fitted for determining water in gases, liquids and solids.

The colorimetric titration helps in detecting free water, dissolved water, and emulsified water.

It is a swift process which demands a minimal amount of sample preparation.

It is extremely accurate method.