D.N.R.COLLEGE (AUTONOMOUS): BHIMAVARAM

DEPARTMENT OF PG CHEMISTRY

QUALITY CONTROL AND TRADITIONAL METHODS ANALYSIS – I

Presented by

T. MOUNICA

DNR COLLEGE BHIMAVARAM

UNIT – I

QUALITY CONTROL IN ANALYTICAL CHEMISTRY

CHARACTERISTICS OF AN ANALYSIS:-

Quality of an Analytical Procedure:-

Limit of detection: - (lowest concentration of the analyte that can be reliably detected)

All instruments having some degree of noise due to any impurities present in the sample. It is reduced by LOD values.

LOD may be defined as the difference between the signal concentration of analyte and signal concentration of blank, which is equal to the 3 times of standard deviation of blank.

$$X_A – X_B = 3S_B$$

Here,

X_A = Concentration of analyte signal

X_B = Signal of blank

S_B = Standard deviation of the blank readings.

Trace method is defined as the difference between signal concentration of analyte and signal concentration of blank. This is equal to the 10 times of standard deviation of blank.

$$X_A-X_B = 10S_B$$

Then the signal to noise ratio is greater than 5. LOD is the lowest concentration level that can be determined to be statistically different from a blank (99%).

Sensitivity:-

It is defined as the ratio of the change in instrumental responds (i.e, Signal Io) to a corresponding change in the stimulate concentration of the analyte (C).

$$S = \frac{dI_O}{d_C}$$

Here,

dI_O = change in the instrumental respond

d_C = change in the concentration of analyte

Sensitivity expressed in micro organisms per milli liter of analyte. That produce an absorbance is 0.0043nm. To measure the samples of closely related concentration at the high intermediate and low concentration.

Safety:-

All analytical instruments are quality control instruments and salts and solutions are to preserve the safely in position of laboratories and industries.

Cost measurability:-

Analytical costs are expressed as some of many per results less often in man hours. These are three types,

i) Personal cost:-

These cost related to the safety of the operators, laboratory staff and environment and comfort of the staff.

ii) Over head cost:-

These cost are arises from the laboratory set up and maintained purchase of maintained of equipment and salaries of the staff.

iii) Specific cost:-

These cost are arises from the damage any equipment and product loss sudden accidental fires.

Selectivity and Specificity:-

Selectivity: -

It is a basic property defined as the ability to produce results exclusively depends on the analyte. For it's their identification of the sample. There are many types of analytical inference as chemical, physical, instrumental. Quantification of method of selectivity based up on,

i) Maximum tolerated ratio (T_R):-

It is ratio of Concentration of interference and Concentration of analyte.

$$T_R = \frac{C_{\text{Interference}}}{C_{\text{Analyte}}}$$

ii) Sensitivity ratio (S_R):-

It is a ratio of signal of analyte and signal of interference.

$$S_R = \frac{S_{\text{Analyte}}}{S_{\text{Interference}}}$$

iii) Selectivity ratio factor (S_P):-

It has two tolerated ratios the ratio between the first tolerated ratio and second tolerated ratio is called selectivity factor

$$S_R = \frac{[TR]_1}{[TR]_2}$$

Specificity:-

Analytical specificity is the ability of the experimental process to register only analyte. There by other components or characteristics present in the sample do not influence that analytical result. Specificity is the ultimate of selectivity.

Quality control – Principles of Ruggedness test:-

It is a analytical method is the degree of reproducibility of test results obtained by the analysis of the same samples under a variety of conditions, such as different laboratories different analyst, different instruments, different lots of reagents, different elapsed assay times, different assay temperatures, different days.

The ruggedness of an analytical method is the resistance to change of an analytical method when minor deviations are made in the experimental conditions of the procedure.

The aspects of the method which are susceptible to minor deviations in the experimental conditions of the procedure should be indentified and their influence on method performance evaluated using ruggedness tests.

The ruggedness of a method is tested by deliberately introducing small changes to the method and examining the effect on particular aspects of performance. A large number of aspects of the method may need to be considered but because most of these will have a negligible effect it will normally be possible to vary several at once. An approach utilizing 8 combinations of 7 variable factors has been desired by youden.

Some of the ruggedness parameters that a method should be evaluated for are:

Changes in instrument, operators, laboratories,

Brands (or) chemicals and supplies.

Slight changes in solution concentration (or) sample preparation parameters

E.g. pH, extraction time change in temperature.

In addition, the stability of the standard and simple preparations must be assessed to determine the speed at which the analysis should be performed.

Robustness test:-

It is an analytical procedure is a measure of its capacity to remain unaffected by small, but deliberate variations in method parameters and provides an indication of its reliability during normal usage.

Determination-the evaluation of robustness should be considered during the development phase and depends on the type of procedure under study.

Difference between Ruggedness test and Robustness test:-

Along the similar lines it has been suggested that ruggedness should be used as a parameters evaluating constancy of the results when external factors such as analyst, laboratory, instrument, reagents and days are varied and robustness should be used as a parameters characterizing the stability of the method respect.

Unaffected by small variations in the method parameters (mobile phase composition, column age, column temperature and influential environmental factors (room temperature, air, humidity).

Solubility of analytical solutions, extraction time.

Verification of stability of analytical solutions in importance.

Liquid chromatography-robustness includes, flow rate.

Control charts:-

A control chart is a graphical representation of collected information which enables the quality characteristics.

No process can turns identical products unit to unit, hour to hour to hour, day to day. The variation observed in product reflex variable material process operator and other causes.

At best one can try to keep the variability within the to meet the requirement of the specimen limits. The process inspection is best accomplutation by using control charts.

It may be day by day plot of the average moisture contain of gain sample or concentration of a sample solution or the percentage of concentration in successive a plots.

The control units oh the characters so placed as disclosed the presence (or) absence of the assignable of quality variations. The following types of control charts are used in analytical quality assurance.

i) Stewart control chart

ii) X –Chart

iii) Recovery rate control chart (R-R) chart

iv) Rate control chat(R- chart)

v) X-R combination chart

vi) Standard deviation chart

vii) Difference chart

viii) C (Cusum) - charts

i) Construction of Stewart chart:-

In a Stewart chart contains unit of the results and these divided corresponding the X – axis is a desecrates sequences axis on which the time, series number take (or) concentration recorded.

The results of the preliminary period are them entered consequently often ‘n’ days mean is R – bar and standard deviation calculate.

In Stewart chart center of the line represented by calculated mean value.

Using the standard deviating warning and control units X±2S, X±3S.

Upper control limit X+3S

Lower control limit X-3S

Upper warning limit X+ 2S

Lower warning limit X-2S

Out of control situations:-

Six consequent values on the one side of the central line. Another six consequence values on the central line it is having good accuracy.

Four consequences values to decreasing tendency to lower volume to decreasing tendency to lower volume limit in this case precision will be occurred.

S. No	Name of the Chart	Determinations	Error
1	Stewart chart	Mean, standard deviation, accuracy, precision	Random errors, gross error, and system errors
2	X-Chart	Mean, standard deviation, accuracy, T – test	Gross error
3	R- R chart	Mean, standard deviation	Random errors
4	R-Chart	Mean, standard deviation	Random errors
5	X-R chart	Mean, standard deviation, accuracy	Gross error
6	Standard deviation	Mean, standard deviation, accuracy, precision	Random errors, gross error
7	Difference chart	Mean, standard deviation, accuracy	Gross error, random error
8	C chart	Mean, standard deviation	Gross error, random error

Youden plot:-

In this method for the exclusion and evolution of inter laboratory test. It is a simple statistical method for obtaining information about precision and systematic errors. From analytical results without much effect only to additional samples must be analyzed once. The inter lab test is evaluated graphically by plotting the results as youden plot.

Applications:-

External analytical quality assurance:-

To compare analytical results that is for monitoring the accuracy. To compare analytical process suitability. When comparing the process one can also detect systematic errors of analytical process.

Internal analytical quality assurance:-

Precision and accuracy controlling place of control charts.

To compare the performance of different operators.

Ranking test:-

The Wilcoxon rank sum test is used to test for a difference between two samples. It is the nonparametric comparing to the two samples Z (or) T test. Instead of comparing two pollution means, we compare two population medians.

Evolution and reliability of analytical data:

Limitation of analytical methods:-

Accuracy:-

The difference between the experimental (or) observed value and the true most probable value is called absolute error of the determination.

Accuracy is expressed inters of the absolute error of the quality under measurements or as the degree of agreement between measured value and true value. The true value value is never known to the degree of 100% accuracy.

Ex: - the measured value of iron in a sample is 20.44% while the sample accurately contains 20.34.

Absolute error = Measured – True value

$$\text{Accuracy} = \frac{\text{Absolute error}}{\text{True value}}$$

$$= \frac{20.44-20.34}{20.34}$$

$$= \frac{0.10}{20.34}$$

$$= 0.0049$$

Relative accuracy error:-

$$= \frac{\text{Absolute error}}{\text{True value}} \times 100$$

$$= 0.0049 \times 100$$

$$= 0.49\%$$

Precision:-

It is defined as the degree of agreement between numerical value and other value of measurements precision is used to describe the reproducibility of the results. It also employs nothing about their true value.

It is the close agreement of values among a group of experimental results carried out by different persons on the same method bys different persons on different methods on the same measurements.

The results may show a high degree of precision or food argument with one another.

Errors in chemical analysis:-

Errors:-

It is defined as the numerical difference between the measured value and true value.

Classification of errors:-

Errors are classified in to 3 general groups based on the nature of their occurrence.

i) Gross error:-

These are mistakes that are not likely to be repeated in similar determination.

Spilling a portion of the sample.

Recording the long value for one of the weight used.

Fluctuation in the balance room.

Ex;-

Wind shaking of the table, reading the wrong volume of liquid in a burette, simple mistakes in the arithmetic combination then the decimal point is misplaced in the recording. Failure to execute some essential step in the procedure.

Minimization of grass error:-

Repeating the measurements at least thrice, for excessively complicated measurements a checklist prepared a shade of time.

Making sure that liable clear and the scales are clear. Keep the experimental set up as orderly.

ii) Systematic or determinate errors:-

They can be ascribed to definite causes they are unit directional with respective to the true value. Determination errors are often reproducing.

They can be predicted by experimental operators.

These are classified in to 4 types.

a) Instrumental (or) Repeated errors:-

These errors are arises from the in accuracy on the part of the instrument, equipment, glass ware, impurities in the chemicals.

UN certain reading an instrument scale or measuring system. Uncalibration or improperly calibrated and facility balance weights.

Balance arms unequal lance .purely or in correctly graduated glass ware. Impurities in reagents. Pure selection equipment.

Loss of weight of platinum crucible strongly heated. Failure to properly establish a zero readings of the instrument scale.

Minimization of instrumental or repeat errors:-

Centering in reading an instrument scale or measuring system. Calibrated reagents calibrated glass wires are used

Balance arms are equal. Correctly glass ware, correct section equipment, pure reagents.

Stable platinum crucible are used, any instrument is used to adjust the zero value.

b) Methodical error:-

These errors are raised from the basically they originates from in cut sampling and from incompleteness of a reaction, methodical are causing the following ways.

In a gravimetric analysis errors arise owing to the solubility of precipitates co precipitation, decomposition, post precipitation and volatilization.

Ex: - When Ca^{+2} ions are precipitated as calcium oxalate washing precipitate results in a loss of substance due to solubility leading to an error in the net weight.

Simultaneous co precipitation post precipitation effects. Linkage of material or electrically in electrical circuit.

Minimization of methodical error:-

Before going to the analysis the sample must be in the form of dried form after it is accurately weighed. We check the any impurities present in the sample or glass containers.

Before going to the analysis we knew the theoretical knowledge of required sample analysis. We observed the any side reaction in the analysis.

c) Personal (or) Operative error:-

These errors are aroused by personal mistakes in the analysis. Some personal are given below. Poor color precipitation.

Consistent par all error in reading scales (or) burette.

Loss of precipitation.

Minimization of personal error:-

Visible the correct end point. We conduct the clear end point titrations.

The process is completed in exact time. The foreign sample stored in a tight covered beaker in a insert medium. We observed correct identification reactions.

d) Constant additive and proportional error:-

When the magnetic determination error is nearly constant in a series of analysis regardless of size of the sample or independent of the amount to be determined is called as constant additive error.

Error in weight. Loss of weight a crucible in which a precipitate is ignited.

Minimization of constant additive error:-

We have to use the minimum sufficient large amount of the sample is used for the analysis.

iii) Intermediate error:-

Noise and drift in an electric current.

Temperature vibration. Accidental loss material during analysis.

Vibration in a caused by moving tropic.

Significant figures:-

Significant figures avoid the expression of results to digits are misleading maintaining for the final product and indication of the precision or uncertainty of values contributing to the calculation of results.

Volumetric correction:-

Dilution law calculation volume shows 12.3mL here significant figure is 2 which is less than 5. So final reading is represented final reading 12.3mL.

For in case volume shows 12.38mL here significant figure is greater than 5.

Weight correction:-

In weight calculation weight shows 1.32524g here significant figure is 4 which are less than 5.so correction weight is 1.3252.

For in case weight represents 1.32528g the fifth digit significant is 8 which is greater than 5 so correction weight is 1.3253g

Quality assurance and management systems:-

ISO series of standards 9000 & 14000:-

Basic concepts of ISO 9000:-

ISO-International Organization for Standardization (or) International Standards for Organization

It is the series of ISO 9000, ISO 9001, ISO 9002, ISO 9003, ISO 9004 interrelated by quality, management and quality assurance system.

ISO 9001, ISO 9002, ISO 9003 models for external quality assurance system.

ISO 9001 give the guidance for covering design, development, manufacturing, installation and serving system.

ISO 9002 give the guidelines for only covers precaution and installation.

ISO 9003 give the guidelines for cover only finally product and inspections and testes.

ISO 9001, ISO9002, ISO9003 construal situation between costumer and supplier.

ISO 9004 give the guidelines for manufacturing development its own quality system to need the business leads.

Finally ISO 9000 gives the quality systems guiding building quality in to product of services.

Basic concepts of ISO 14000:-

After the success of ISO 9000 series ISO provides ISO 1400 which cover the overall statistic energy from the environmental agency.

It cans ISO 14000 series association as environmental manage mental and environmental adulating.

Europine unions introduced terms environmental management and environmental adulating.

USA, Japan, jarman introduced ECO labeling.

ISO 14000 series of standards series design to cover the,

i) Environmental management system

ii) Environmental adulating

iii) Environmental labeling

iv) Environmental performance and evolution

v) Life cycle assignment

vi) Environmental accepts and produces.

ISO 14000 constituent’s series are like-

ISO14000,ISO14001,ISO14010,ISO14011,ISO14012,ISO14013,ISO14020,ISO14024,ISO14031,ISO14040,ISO14050.

ISO 14000 give the guidelines for environmental system.

ISO 14010, ISO14011, ISO14012 gives the guide lines for environmental adulating.

ISO 14020, ISO14024 give the guide lines for environmental labeling.

ISO 14031 give the guidelines for environmental performance and evaluation.

ISO 14040 it gives the guide lines for life cycle assessment.

ISO 14050 give the guide lines for environmental accepts and products.

Good laboratory practices (GLP):-

The exact definition of GLP depends on who is defending it and what purpose.

A broad definition is such issues as of the organization of the laboratory management personal, facility, equipment, operation method valuation, quality assurance, record.

A goal is certified that every step of the analysis is valid.

GLP was first officially using the year 1972 by Newsland testing laboratory after Thalamide disaster, regularity, and safety and testing of pharmaceutical industries.

Organizations:-

USFDA – united state food and drug authority, which give guidance for quality product, safety, and testing, toxic metals.

USEPA – united state environmental protection agency.

OECD – organization for economic cooperation development, which is inter governmental organization with 29 industrial countries, North America, Europe and pacific etc.

GLP have been established by worldwide bodies such as the organization for OECD and the international organization for standardizations.

Government agencies adopted them for their purpose as rules that must be followed for laboratory involved in analyzing substances the required regulations.

GLP can be defined as a body rules operating procedure and practices established by given organization that are consider to be mandatory with a view to insuring quality and correctness in the results producing by laboratory.

They are containing two common elements:-

i) Quality assurance:-

It is defined as although planed a systematic action provides that product stratifies all requirements.

It is quality measurements systems which is organizing overall activities of the company.

ii) Standard operating procedure:-

It provides details descriptions of activities performed by the laboratory.

Ex: -

Sample custodies, sample handling, sample preparation, instrument maintained and recorded.

GLP status in India:-

In India laboratory which conduct study in cordianece which GLP principle.

Indian laboratory mans proposing the none of the Indian government developments have any GLP certificates.

Brief out line of ICH guide lines in drug substances and products:-

International conference on harmonization of technical requirements for registration of pharmaceutical for human use (ICH):-

The ICH is a project that brings together the regularity authorities of Europine Japan and the United States and experts from the pharmaceutical industry in the three regions to discuss scientific and technical aspects of pharmaceutical product registration.

The purpose of ICH is to reduce the need to duplicate the testing carried out during the research and development of new medicines by recommending way to achieve greater harmonization in the interpretation and applications of technical guidelines and requirements of product registration.

Harmonization would lead to a more economical use of human, animal and material resources and the elimination of unnecessary delay in the global developments and availability of new medicinal while maintaining safe guides on quality, safety and efficiency and regularity ailing to protect public health.

ICH guide lines have been adopted as law in several counters but are only used as guidelines for the united state food and drug administration’s (USFDA).

In the 1980 what is today the Europeans union began harmonizing regulatory requirements. In 1989 European, Japan and the United States began curtaining plans for harmonization ICH was excreted in April 1990 at a meeting in Brussels Europeans.

Process:-

The ICH process consists of **five** steps.

1) Expert working group consensus building:-

When the screening commute (SC) adopts a concept paper as anew topic the process of consensus building begins a reporter is usually designated from the industry member of the respective six member expert working group. the EWG consists of regularity and industry parties and observers the reporters prepares are initial draft of the guideline based on the objectives set out in the concept paper and in conclusion with experts designed to the EWG.

2) Conformation of EWG consensus by the SC:-

It is reacted when the SC aggress based on the report of the EWG that there is sufficient scientific consensus on the technical issues for the draft guidelines this text is signed off by SC as step 2 final document.

3) Regularity consultation and discussion:-

The draft becomes subject of consultation in the three regions. It is published in the European, Japan and USA and everybody with in there region can committee on it. There is also an opportunity for committee on the draft when is distributed by IFPMA and WHO. The draft document to be generated as a result of step 3 phase is called experts document.

4) Adoption of an ICH harmonized guideline:-

It is final document is signed off by SC Signatories for the regularity part is of ICH an ICH harmonized tripartite guideline.

5) Implementation:-

Information on the regularity action taken and implementation dates are reported back to the SC and published by the ICH secretariat on the ICH website.

UNIT – II

DECOMPOSITION TECHNIQUES IN ANALYSIS

a) Inorganic compounds:-

Decomposition:-

When a single compound breaks down into two or more elements or new compounds. These reactions often involve an energy source such as heat, light or electricity that breaks apart the bonds of compounds. For example,

$$AB \rightarrow A+B$$

$$CaCO_3 \rightarrow CaO+CO_2$$

Dissolution:-

In this process where a solute in gaseous, liquid, or solid phase dissolves in a solvent to form a solution. Solubility is the maximum concentration of a solute that can dissolve in a solvent at a given temperature.

Stirring sugar into water is an example of dissolving. The sugar is the solute, while the water is the solvent. Dissolving salt in water is an example of dissolution of ionic compound. The sodium chloride (salt) dissociates into sodium and chloride ions when it is mixed with water.

Principle of decomposition and Dissolution:-

Decomposition:-

Some chlorides of metals like AgCl, $HgCl_2$ etc.

Some metal carbonates i.e.; $CaCO_3$, $MgCO_3$, SrO_3 and some sulphates of metals like CdS, $ZnSO_4$, $NiSO_4$.

These are in soluble in water; these are decomposing by using suitable solvent.

Definition:-

To bring the solid substance in to solution by dissolving in suitable solvents like acids – HCl, H_2S2O_4, HF……here the nature of the reactants will be changed.

$$CdS+2HCl \rightarrow Cd^{+2}+2Cl^{-}+H_2S$$

$$CaCO_3+2HCl \rightarrow Ca^{+2}+2Cl^{-}+CO_2+H_2O$$

The decomposition of CdS, the sulphide ions escaped as H_2S from the solution.

The decomposition of $CaCO_3$, the sulphide ions escaped as CO_2 from the solution, the nature of $CaCO_3$ is Changed.

Dissolution:-

It can be defined as to bring the solid substance in to by dissolving suitable solvent. The nature of reactance does not change.

Ex: - $NaCl \rightarrow [Na^{+} Cl^{-}] \rightarrow [Na^{+} Cl^{-}]$

In order to analyze we have to select the correct parameters of the substance and we have to select the substance in to solution form. We choose solution form for analysis, because in gases form reactions are fast and in solid form reactions are very slow and also we use number of methods in solution form.

$$NaCl+AgNO_3 \rightarrow AgCl+NaNO_3$$

$$CaCl_2+EDTA \rightarrow Ca\text{-}EDTA$$

Difference between dissolution and decomposition of organic and inorganic substances:-

S.NO	Organic compounds	Inorganic compounds
1	Organic compounds usually do not dissolve in water.	Inorganic compounds usually dissolve in water.
2	Organic compounds generally dissolve in organic solvents like ether, alcohol, benzene and chloroform.	Inorganic compounds generally do not dissolve in organic solvents.
3	Organic compounds have usually low melting points and boiling points; and they usually decompose on heating.	Inorganic compounds have usually had high melting points and boiling points; and they usually do not decompose on heating.
4	Organic compounds are inflammable; they catch fire easily.	Inorganic compounds are usually non inflammable; they do not burn easily.
5	Organic compounds exist as covalent molecules, so they are non- electrolytes.	Most of the inorganic compounds are ionic, so they are electrolytes.

Importance of decomposition techniques in analysis:-

It is an important part of combined procedures for the determination of trace elements in solid samples. After a short summary of the potential sources for systematic errors two new decomposition methods are described that are suitable for the ashing of organic environmental samples.

Principle of dissolution of an inorganic substance:-

Polarity and Purity of solvents:-

Normally we use water as solvent per dissolution purpose because it has high polarity combined to others.

Normally we use distilled water because tap water contains number of cations and anions.

Then the main factors which influence dissolution or attraction between the species and salvation of water.

For example if we take NaCl salt it is in solid form when sufficient amount of solvent is added to the solid NaCl. Then which is dissolved solid NaCl is converted in to liquid state by the solution of ions.

The ions $Na^+ + Cl^-$ surrounded by water molecules.

Each Na^+ and Cl^- ions arrounded by 4 or 6 or 8 water molecules.

The concentration of solid or salt increases then the solubility of the substance decrease in the solvent.

The attraction between Cl^- and Na^+ ions in the water decreases they can’t close together in water.

The solubility of AgCl is 10^{-12} times less than the NaCl in water.

AgCl is decomposed by adding ammonia to the substance. Thus Ag^+ ions present in Agcl form complex with NH_3.

$$AgCl+NH_3 \rightarrow [Ag\ (NH_3)2Cl^-]$$

Properties of solvents:-

Dissolution and Decomposition of the components depends on temperature, pressure, H^+ ion concentration, polarity of solvents, and anion of the acid.

Temperature:-

If we take water for dissolution of components, we need up to its boiling point 100^0c.

If we increase the temperature, then the monomers of the water molecules increase by the breaking of the hydrogen bonds in the water molecules.

The solution of the ions increases consequently the solubility of the components also increases.

If we take water we need to up to only 100^0c.

Above 100^0c water molecules evaporated from the solution.

If we take acids for the decomposition of the substance we need up to its boiling points of acids is greater than water.

Pressure:-

If we increase the pressure hen molecules are compounds close together.

Decomposition of samples with acids:-

Decomposition of H_2O:-

Water molecules can be broken down into hydrogen and oxygen molecules by a chemical reaction called electrolysis.

When an electric current is passed through liquid water (H_2O), it changes the water onto two gases- hydrogen and oxygen.

The molecules of water break apart into individual atoms.

Electrolysis of water is the decomposition of water (H_2O) into oxygen (O_2) and hydrogen (H_2) due to an electric current being passed through the water.

Decomposition of HCL:-

The lab normality of HCL is 11.6N.

The anion (Cl^-) present in the HCL. Acts as a mild reducing agent.

The boiling point of HCL is 110^0C and chloride ion in the HCL to acts as a complexing agent.

The concentration of HCL is an excellent solvent for in organic samples.

It is the basic solvents for the analysis of ores and minerals.

It is easily volatile most of the most are soluble and it is also having weak reducing power.

Antimony, Sn, Hg, Germanium these are volatile compounds with HCL.

HCL is a strong acid which forms complexes with iron.

Eg: - $[FeCL_4]^{2-}$, $[FeCL_6]^{-3}$

The decomposition of HCL is generally carried out in a glass vessel.

If we take Platinum or Gold vessels, they are may be carried due to the prolong contact with HCL.

Dissolution of heavy metal like carbonates is done by using Concentration HCL.

The Oxides of iron and Manganese are dissolved in HCL.

Sulphides of several metals are also soluble by using HCL.

Ores of Zn, Ba, Sn, Ca are dissolved in concentration of HCL.

Boron ores are also decomposing using HCL at eliminated temperature.

The salts of Sulphides, Phosphates, Chlorides, Hydroxide ions are also soluble in HCL.

Minerals of Thorium, Uranium are also decomposed by using concentration of HCL which are present at phosphate.

Vanadates, Arsenates, Tungstates etc. are also easily decomposed by HCL.

Decomposition of HF:-

The lab normality of HF is 29N.

The boiling point of HF is 113^0c.

Fluoride acts as a complexing agent in HF.

In decomposition of minerals and ores hydro fluoride acid has an effect greatly from other mineral acid.

It reacts with silicates or SiO_2 it gives unstable H_2SiF_6.

Which dissociated gives SiF_4.

HF dissociates to very less exchange in water and forms HF_2O type of ions in water molecule.

The fluoride ions forms complexes with several metal ions like- V, B, Al, Fe, Ni, Th, Sb, Ge, Se, Mb, W.

HF can be stored in polyethylene and Teflon vessels.

Fluorides of several metals especially that of fourth group volatile.

In analysis of Silicates mixture of hydrofluoric acids and minerals acids (HF & H_2SO_4) are used.

Certain metals ions also form Fluoro compounds like Fluoro Borate and Fluoro Aluminates etc...

For the decomposition of fluoro pellets measure of mixture of HF and $HClO_4$ in ratio 1:1 be use at elevated temperature.

The temperature can be increase up to 200^0c in Teflon beaker or Teflon coated metal system.

If we use metal containers it will interact with HF and $HCLO_4$.

Dissolution of silicates in HF is generally used for the decomposition of trace method and for their estimation.

Decomposition of HHO_3:-

The lab normality of HNO_3 is 16N.

Decomposition of substance depends up on H^+ ion concentration and NO^{3-} ion act as oxidizing agent.

The concentrated HNO_3 is a strong oxidant that dissolves all common metals like Alumina and Chromium.

The alloy congaing Sn, Tungsten, Antimony are treated with concentration HNO_3.

Hot HNO_3 allow ore in combination with other acids and oxidizing agents such as H_2O_2, Br_2. It is widely used to compose organic samples for determination of their metal compound.

HNO_3 is a strong acid and also act as strong oxidant; it is oxidize several species to higher oxidation state like sulphides to sulphur and sulphtes.

It is generally stored in poly ethylene and glass and Teflon.

Gold, Platinum, Uranium, Thorium do not dissolved easily in HNO_3.

Where Ag, Pd are easily soluble in HNO_3 majority of metals decompose with HNO_3, except Gold and Platinum.

The decompose of copper over HNO_3 is best acidic medium.

The presence of NO^{3-} can be removed by repeated evaporation by the same process applying the H_2SO_4.

Minerals contains Bi, Sn also decompose very easily concentration HNO_3.

Decomposition of H_2SO_4:-

The commercially normality (lab) of H_2SO_4 is 36N.

The boiling point if H_2SO_4 is 338^0c.

The sulphate ions in H_2SO_4 act as complexing agent.

Many materials are decomposed by concentration of H_2SO_4.

Most of the organic compounds are dehydrated and oxidize at this temperature.

Sulphate ions also form complex with several metal ions and tetravalent in higher concentration.

Sulphate ions are weak oxidizing agents.

It is also stored in glass vessels even in higher concentration.

It can also store in polyethylene vessels up to 50^0c.

Teflon is resistance up to 300^0c.

Platinum or gold are also carried with H_2SO_4.

It is sufficient solvent for a number of metals like sulphides, Chloro silicates, Niobium, Titanium, Zirconium etc…

It is also used in hot conditions to decomposing poly metallic ores like Barium, Lead.

It is very suitable solvent or decomposing minerals containing the Selenium, Tellurium.

Very slow volatilization the H_2SO_4 is the best decomposition solvent for the rare earth elements.

Phosphate containing Thorium, Titanium, Niobium and Lanthanum are dissolved in H_2SO_4.

Decomposition of $HClO_4$:-

The lab normality of $HClO_4$ is 11.4N.

The boiling point of $HClO_4$ is 203^0c.

The ClO_4 ions acts are very oxidizing agent in $HClO_4$.

Perchloric acid is very strong acid. It is very high boiling point by compared to other mineral acid.

Most of per chlorides are suitable except P, Sb, Rb, these are soluble.

Determination of salicylic acid or silicates in complex materials possible by decomposing with per chloric acid.

All which minerals can be decomposed.

Efficiently by using PerChloric acid.

For the decomposition of phosphates, we must like HNO_3 and $HClO_4$.

Monosides can be decomposed more efficiently by taking a mixture of H_2SO_4 and $HCLO_4$.

Minerals like Cr, Zn, Ti, V and their oxides or silicates decompose by taking $HClO_4$ and H_2SO_4.

The decompose of lea sulphide is faster. If concentrated $HClO_4$ than HNO_3.HCL.

Barium containing ores decomposed by taking HCL + $HCLO_4$ or H_2SO_4 and $HClO_4$.

Fusion:-

Fusion is a dry decomposition technique if we take acids. The decomposition of the components we can need up to its boiling points only. The components in soluble in acids.

Such type of components decomposed by using fusion and sintering methods.

The sample is mixed thoroughly fusion materials like Potassium Pyro Sulphate, NaOH and Na_2CO_3 and heated to 900-1200^0C per 15-45 min.

In fusion technique the ratio of fusion material is 1:10 or 1:25.

In fusion technique initially the fusion materials converted into liquid state at its melting point. The converted fusion materials react with sample.

Generally metal silicates ‘U’ and Th ions decomposed by using fusion technique.

M-Silicates+Na_2CO_3→M-CO_3+Na-Silicates→solution→add dilute acids

Advantages:-

Sodium does not react with sample.

The melting point of Na_2CO_3 is 813^0C.

Metal silicates react with Na_2CO_3 converts to sodium silicates which are soluble in nature and also metal carbonates are insoluble in nature.

So we can eliminate carbonate easily from out solution.

Vessels:-

Glass and quartz these are not used because they cannot stand with high temperature and following vessels are used.

Platinum- 1772^0C.

Nickel -1453^0C.

Copper- 1083^0C.

Gold- 1063^0C.

Silica < 1600^0C.

Silver - 960^0C.

This fusion purpose we required to suitable fusion material and suitable sources of heat, we required heat or temperature up to above 9000C and also we required vessels which can be stand at high temperature.

In this case the time taken for fusion is nearly 15 to 45M.

At higher temperature corrosion taken place due to vigorous reactions.

If we increase time and decrease temperature the interaction between the sample fusion materials to increase consequently efficiently of fusion will also increases.

Sintering:-

A process where the sample mixed thoroughly with selected substance in the ratio 1:1 (or) 1:2 under fine power is heated to lower temperature for a long time.

During this heating process the fine power will slowly becomes a solid. It is called sintering.

The sintered materials are leached with acids which gives soluble and insoluble materials.

Which are later analyzed for different constituents?

Sintering + Sample→ Sample + Na_2CO_3 → Solid Solution→ Insoluble→ Soluble

Time taken for the sintering process 2 to 4 hours and temperature 400-600^0C.

Na_2CO_3 is added to the sample. Initially Na_2CO_3 converted in to liquid.

Then which is reacting with sample simultaneously it may react with walls of the vessels.

In this fusion it is necessary to use 5-15 times higher concentration of fusion mixture to the sample.

This introduces the problem of purity of the sample used for fusion mixture.

After consider the above mentioned problem scientist tried to minimize the temperature and increase time of interaction between solids and also simultaneously reduce the amount of materials to be mixed with the sample and developed sinter.

In introduce the problem of fusion but simultaneously enhance the efficiently of decomposition.

Depending up on the nature of the ore or minerals the condition like amount of material used for sintering, temperature and time for sintering are selected.

In the sintering process the reaction between the sample and sintering materials takes place in the solid state. Only at the temperature used and time selected.

Difference between Fusion and Sintering:-

S.NO	Fusion	Sintering
1	Fusion a process where the sample is mixed with and 10 times or 20 times fused mixture and heat up to 900-1200^{0}C.	Sintering is a process where the sample is mixture with almost 2 or 3 times of fusion mixture and heated up to 400-600^{0}C
2	Time of reaction is 15-45min.	Time of reaction is 2 to 4 hours.
3	The liquid fusion mixture is responsible for the decomposition.	Formation of sintered compound takes place.
4	Corrosion of vessel is very high because of high temperature.	Corrosion of vessel is very less because of low temperature.
5	Pt, U can be used as vessels.	Pt, U and also Ni can be used.
6	The size of particles is high compare to the sintering process.	The size of particles is high is less compare to the fusion process.
7	We used very pure fusion mixture to avoid contamination.	Here also we must use very pure sintering materials.
8	Amount of fusion materials is very high in fusion techniques.	Amount of sintering materials is compared to the less with fused materials.
9	The interference is very high in case of fusion because we are taking 10 and 25 times are fusion materials.	The interference is very low compare to the fusion techniques.

Decomposition of substance by fusion with Na_2CO_3:-

Anhydrous sodium carbonate is generally used as a fluxes form the decomposition of silicates rocks and minerals.

For oxidative decomposition the amount of fusion mixture should not be large.

It will damage the crucible.

But in case of basic rocks with oxidizing nature excess decomposition fluxes is used

The temperature selection for the fusion also depends upon the nature of the rocks to the decomposition

In the case silicate rocks temperature range of 300-400^{0}c is sufficient but for oxidative rocks temperature range of 700-900^{0}c is required.

After the fusion the mixture form soluble & in soluble salts which are dissolved in either water (or) suitable acids.

Baring minerals easily decomposed by fused into Na_2CO_3 Similarly Zirconium minerals also can be fused with Na_2CO_3.

This (produce) procedure can be utilizing for the determination of Fe & U. This is present in very low concentrations in Zirconium Phosphate ore's & Silicate ores.

In the case of Aluminum minerals are ore's addition of Na_2CO_3 will need to perfect minerals decomposition of the minerals at the high concentration of Aluminum.

The minerals of Titanium can also decomposed easily by Na_2CO_3 fusion.

Decomposition of substance by fusion with NaOH:-

Fused NaOH melt at 328^{0}c at the Hydroxide ions one Na & Potassium (different variable amount of water) liberate variable amount of water by fused. They melt as fumes then it is allowed to fuse alone & after cooling in suitable weighed amount of powder sample in introduced into melt & fusion processes is continued.

The fusion with hydroxide in generally useful decomposes Quartz, Silicate, and Sand. Clay Silicate & Carbonates are many metals natural Oxidants, Titanates, Tungstates, Florets can also be decomposed with NaOH fused mixture.

Iron (or) Nickel crucibles are used they are cheaper then platinum crucibles.

Teflon can also be used if fusion temperature is less than 300^{0}c.

Fusion of Quartz glass with hydroxide mixture reacts quickly forming water soluble compounds.

Titanium contain like Titanates can also be fused with NaOH which form alkaline sodium Titanate type of compounds.

Minerals of Aluminum including Bauxite required not only NaOH but small quantity of Na_2CO_3 for complete determination up to 97%.

Minerals contains stagnates also behaved similarly.

Chromates, Bromides can also be decomposed by used NaOH.

For the process of decomposition can be completed only after the adding Na_2O_2 type oxidizing agent. Why because in case of Chromites there are less soluble than Chromates.

The decomposition of Silicates, Molybdates, Tungstates, and Zirconates is always preferable to use NaOH & Na_2O_2 decomposition mixture.

Decomposition of Phosphate & Fluoride minerals containing Silicates are easily decomposed by NaOH fusion.

The decomposition of Phosphates & Fluoride in more completes then that of Na_2CO_3.

Decomposition with Sintering by with Na_2O_2:-

It is also used as the fusing mixture but there are serious problems of the vessels crucibles.

Samples are decomposed by sintering processes using Na_2O_2 in platinum crucibles.

Platinum corrodes very little the temperature should be kept below 500^0c always so that the corrosion of the vessels is completely prevented.

The mixtures like Bromide, Zirconium, and Aluminates are decomposed efficiency in range of 250^0-300^0c.

SnO_2, ZnS, Al_2O_3 are decomposed by using Na_2O_2.

$$2SnO_2 + 2Na_2O_2 \longrightarrow 2Na_2SnO_3$$

$$ZnS + 4Na_2O_2 \longrightarrow ZnSO_4 + 4Na_2O$$

$$2Al_2O_3 + 2Na_2O_2 \longrightarrow 4NaAlO_3 + H_2O + O_2$$

Decomposition of sintering with Na_2CO_3:-

Sulphates along with Carbonates are quantitative sintering with Na_2CO_3 & small amount of KNO_3.

Sulphates can be estimated by using Gravimetric Procedure.

For lime stone decomposition sintering process with Sodium Carbonate is much more efficient then fusion processer.

Platinum& Palladium can decompose by using mixture of Na_2CO_3 & Sodium Nitrate.

Manganese ores also decomposed by sintering with Na_2CO_3 by taking in a strain less steel crucibles.

Nickel vessels (or) crucibles are present in this situation.

Decomposition techniques (or) Methods:-

These are classified in to 2 types.

I) Open decomposition technique:-

In convention heating we heat the sampling open conditions (i.e. at open atmosphere) & the time taking for heating is large. Hence some contaminates from atmosphere (like dust etc). May come in to corrosion may takes place open digestion requires attention of Analyte (operator), still & experience &continuous.

To avoid these disadvantages we have to go for closed decomposition.

II) Closed decomposition technique:-

In this case we flow the system using lead on the vessel. So there is no contamination from the out-side atmosphere and also it’s requires 5-15 min for heating.

So cost of Analysis is decrease compared to open decomposition technique (or) convention heating.

One more advantage is there is a pressure development (This will increase decomposition of sample).

Note:-

Decomposition will increase if we increase temperature & pressure simultaneously.

Parameters needs to be consider in decomposing the samples for Analysis:-

I) Amount of the material could be taken weighed:-

It is depending on the Analyte i.e. whether it is major, minor trace (or) ultra trace quality.

In case of the Analysis ‘Fe’ here to take small amount of sample. Because ‘Fe’ here is major constituents.

In case of trace Analysis we have to take large amount of sample.

II) Selection of vessels:-

Depending up on the amount of sample we have to choose correct vessel.

In this case we have to consider volume of vessel & nature of vessel (size).

III) Selection of decomposing agent:-

In this case we have to consider purity, concentration & also characteristics of Anions of that agent.

IV) Selection of temperature:-

We should know the temperature of the decomposition and also we should know the melting point of fusion material.

V) Time:-

If we increase the time of Analysis the cost of Analysis will increase. Because we waste regents &also the impurities we use more acids & also increasing the impurities.

VI) Contamination from the vessel:-

Time & temperature & also nature of decomposing materials will influence contamination from the vessel.

Disadvantages of open digestion (or) open decomposition techniques:-

*Long decomposing time:-

The time increases from the solvent (i.e.; Acid)

The time required for decomposition of 30 min to 5 hours accuracy also affected.

Chlorides of Germanium, Calcium, As, Antimony, Hg, and Sn have boiling point. If we use HCL in the analysis of metal. These may from corresponding chlorides may escape from the solution and heating .So the accuracy effect greatly

*Air Burn Contamination:-

In Conventional healing we heat the Sample in Open Conditions i.e. at Open temperature the time taking for heating is large hence some contaminations from atmosphere like dust.

May come into the solution and may affect the accuracy.

* Contamination of Vessel:-

Here corrosion may takes place in open digestion requires attention of sample skill experience continuously.

To avoid these disadvantages we have to go for closed be composition

***Closed decomposition:-**

In this case we close the system using leads to on the vessel so there no contamination from the outside atmosphere and also it's requires 5-15 min heating so cost of analysis decrease compare whit dilution technique.

One more advantage is there is a pressure development this will increase decomposition of the sample.

Absorption of microwave energy heating:-

Micro waves electromagnetic waves that process high frequency and corresponding frequency b/w 300m HZ to 30m HZ [10^6 -10^9] micro waves as expensive use in communication expensively radar, UV and satellite applications.

The most commonly used frequencies for heating purpose are 915m Hz-2456 Hz.

Which correspond to wave length 33.5 and 12.2cm respectively?

This frequencies for chosen through an international agreement to minimize interference with communication services.

Micro wave energy is applied to manual acids, which are directly heated by coupling the reagents with the energy sources.

There are two primary mechanisms for the absorption of micro wave energy its conversion to heat.

I, Dielectric polarization:-

When micro wave irradiation is applied to the sample the electric f magnetic components change rapidly r the molecules cannot respond sufficiently rapidly to the change in direction gives rise to friction and the electromagnetic micro wave energy is converted in to heat. Hence heat is produced due to friction.

How polar molecules in a micro wave field attempt to be orient themselves in accordance with the rapidly changing field

II, Ionic conduction:-

It is another important micro wave heating mechanism.

When a micro wave field is applied to the solution containing anions, they move due to their in hard charge.

As a result anions colloids and the position because the conversion of kinetic energy to the thermal energy.

As a concentration of ions increases in solution more collisions occur causing the solution to get heat faster.

Both these absorption mechanisms have their origin in the alignment of charged [or] partially charged atoms [or] molecules with an applied electric field molecules have the ability to converted micro wave energy in to heat.

Hence heat to produced due to kinetic energy

Micro wave energy is defined as the lasso's tangent.

$$Tan ƒ = \frac{E''}{E'}$$

Where E'and E" are the dielectric constant of dielectric lass respectively.

The dielectric lass define the efficiency of the molecule in convert ting micro wave energy wave energy to thermal heat.

Dielectric constant (E’) is a measure of the ability of molecules to get polar zed to any electric field.

Because both the E’ and E’’ are a function of micro wave frequency.

The lasso’s Tangent is a function of the micro wave frequency.

The lasso’s tangent is a function of the frequency temperature.

Solvent such as mineral acids water f some organic solvent have dipole moment that can interact with applied electric filed.

Ion conduction is lass affect by micro wave frequency for mineral acids both dielectrics polarization f ionic conduction transferring the micro wave energy to heat.

Ultra sonic resisted extraction:-

Ultrasonic energy as be used for wide variety of applications industry, medicine, science.

In analytical chemistry field most applications lie in the capability of ultra sonic to (expand) extract trays analyte from the solid matrix.

Sound wave can induced mechanical titrations in a solid (or) (liquid (or) gas, where as electromagnetic waves can pass through vacuumed.

Ultra sonic as a frequency higher the humans audible range (1-16k.Hz)

Sound waves must travels in the matter as they involve expansions and compression cycles to the medium.

Expansion pulls molecules a part, where as compression pushes that together.

In a liquid the expansion cycle produces negative pressure.

If the ultra sonic is strong inert that that expansion cycle create bubbles (or) cavities in the liquid.

This is so when the negative pressure exceeds the local tensile strength of the liquid which varies depending up on its nature f purity

The process by which vapor bubbles from grow and undergo inclusive colleagues is known as cavitations.

The whole process takes place about 400μ sec.

Caustic cavitations thus provide a unique interaction of energy and matter.

The high temperature r press we produce leads to the formation of free radicals and other Compounds.

In this way the syndication of water (pure) causes thermal dissociation of water molecules in to hydrogen atoms r hydroxide free radicals.

The later forming hydrogen peroxide by recombination.

By use of an acidic exaction combined with ultra sanitation makes the solid particles more flocculent, hence helping the extraction process.

Among the acids employed as extracting as extraction HNO_3 is reported to have an exchanged performance due to its oxidation property.

$$H_2O \rightarrow H+OH$$

$$H+OH \rightarrow H_2O$$

There are 2 common devices for ultrasonic applications namely both and probes units. But ultrasonic probes have the advantage over ultra sonic baths in that.

Their focus their energy on a local sample zone, thereby providing more efficient cavitations in the liquid.

The sonication time required with ultrasonic probes is less (up to 100 times) than that of needed when using ultrasonic baths.

Hence ultrasonic resisted beaching is an effective way of extracting and facilitating with determination of large of Analyst from various environmental samples.

Micro wave & ultrasonic heating are wet decomposition techniques in ultrasonic heating the molecules close together then the normal position.

Hence their exist repulsive forces between them and they go far away.

The attraction forces exist so vibrations takes place in the molecule.

b) Organic compounds:-

Principles of solubility of organ compounds:-

Organic compounds are decomposed by taking organic solvents.

Components are decomposed due to the following forces (or) Intermolecular forces.

I) Dispersion forces (or) London forces (or) Vander wall forces.

II) Dipole – Dipole interactions.

III) Dipole – Included dipole interaction.

IV) Hydrogen bonding.

I) Dispersion forces (or) London forces (or) Vander wall forces:-

Instaneous dipoles are formed b/w 2 non-polar molecules. These are is associated due to electrostatic attractions.

Ex: - CCL_4 & N- hexane

In CCL_4 there is no polar bond & also n –hexane exist without the polar bond.

Dispersion forces are purely physically in nature.

II) Dipole – Dipole Interactions:-

In dipole-dipole interactions dipole of one molecule interact with dipole of another molecule.

The two polar molecules posse’s permanent dipoles.

They interaction between to permanently dipolar molecule increases with increasing dipole character of the molecules.

III) Dipole- Induced Dipole Interactions:-

In dipole induced dipole interaction one polar molecule induces or produces the dipole moment of the non polar molecules.

Polar molecules absorbed on the non polar molecules.

Due to dipole- induced dipole interactions.

Ex:-benzene can react with iodine. Benzene acts as an electron donor and acceptor. It induces the dipole moment to the iodine. Benzene +Iodine, Acetone + Iodine.

IV) Hydrogen bonding:-

Nitrogen, Oxygen, Fluorine is highly electronegative elements.

When they are attached to a hydrogen atom to form covalent bond are shifted towards the more electronegative atom giving rise to a small +ve charge and hydrogen atom and a small –ve charge on the electronegative atom bonded to hydrogen atom.

This partially +ve charged hydrogen atom tends to form a bond with another electronegative atom. This bond is known as hydrogen bond and it is weaker than covalent bond.

For example in HF the hydrogen bond exists between hydrogen atom of one molecule and fluorine atom of another atom.

Hydrogen bond is represented by a dotted line why a solid line represents the covalent bond.

Definition:-

Hydrogen bond is defined as the electrostatic attraction between the positively charged hydrogen atoms in a molecule and negatively charged electronegative atom of the same molecule or another molecule.

Types of hydrogen bonds:-

These are two types of hydrogen bonds

I) Inter molecular hydrogen bond:-

It is formed between two different molecules of the same or different compounds.

For example hydrogen bond in case of alcohol water etc...

For example in hydrogen fluoride the hydrogen bond exists between hydrogen atom of one molecule and fluoride atom of other molecules.

II) Intra molecular hydrogen bonding:-

It is formed when hydrogen atom is in between the two highly electronegative atoms (F, O, and N) present within the same molecule.

For example in O-Nitro phenol the hydrogen atom is in between the two oxygen atoms.

Non polar solvents:-

A liquid solvent without significant partial charges on any atoms as in the hydrocarbon or where the polar bonds are arranged in such a way that the effects of their partial charges all are cancel out. Ex: - Iodine.

Polar solvents:-

A solvent in whose molecular there is a either permanent separation of positive and negative charges or the centers of positive and negative charges are do not in co inside.

Ex: - Alcohols, water, Ketones.

Dipole moments (μ):-

It is defined as the product of magnitude of charge and distance between charges (either +ve and –ve).

μ= charge X distance between +ve and –ve charges.

But in chemistry dipole moment represented by cross arrow.

Re crystallization methods and applications of solubility and Re crystallization:-

It is a purification technique in which crude solid is dissolved in minimum amount of appropriate solvent and sample should be insoluble in solvent at room temperature. But soluble at elevated temperature.

The hot solution is cooled slowly to room temperature either temperature changes the particles are precipitate comes together, leaving soluble impurities in solution. The boiling point of solvent must be less than the melting point of the solute.

The solvent should not react with solute compounds with functional groups. Hydrogen, Carboxylic, Amides will be more soluble. Polar solvents such as water and methyl hydroxide (CH_3OH).

Examples for solvents:-

Inorganic solvents- water

Organic solvents-	Acetic acids	Amides	Alcohols
	Ex:-Acids	Ex:-N-N-Di methyl formamide	Ex:-Ethyl alcohol

Amines-Di ethylene amine

Ether-Di methyl ether

Aromatic compound- Benzene and Toluene

Alkenes- Hexane, Pentane.

UNIT – III

OXIDANT SYSTEMS – PRINCIPLES AND APPLICATIONS IN ANALYSIS

Oxidation:-

Loss of electron is called Oxidation, Loss of Hydrogen and Gain of Oxygen is called Oxidation.

Ex:-Fe (II) →Fe (III) + e^-

Reduction:-

Gain of electrons is called Reduction, Loss of Oxygen and gain of Hydrogen is called Reduction.

Ex:-Fe (III) →Fe (II)

Oxidant:-

Oxidant means itself reduced other substance will be oxidized.

Mn (VII) +Fe (II) →Mn (II) +Fe (III)

Reductant:-

Reductant means itself oxidized other substance will be reduced.

Mn (III) →Mn (II)

Oxidizing agent:-

Cause the oxidation of another substance.

$AgNO_3$ is the oxidizing agent

Reducing agent:-

Cause the reduction of another substance.

Cu is the reducing agent.

Oxidizing agent becomes reduced and the reducing agent becomes oxidized.

$$Cu + 2AgNO_3 \rightarrow CuNO_3 + 2Ag$$

Redox reaction:-

An Oxidation-Reduction is any chemical reaction in which the oxidation number of a molecule, atom, (or) ion changes by gaining (or) losing an electron. The formation of Hydrogen Fluoride is an example of a Redox reaction. We can break the reaction down to analyze the Oxidation and Reduction of reactants.

Oxidant properties:-

Electrode potential:-

The tendency of an electrode to gain (or) loss of the electrons. Then it is contact with its own ion in solution is called electrode potential. It is depends up on nature of the metal concentration and temperature of the solution. There are 3 types, there are,

1) Standard potential:-

The potential is measured at 25^0C, one atmospheric pressure and ions are having unit activity. It is called standard potential.

The E^0 of electrode with 1M (or) 1N solution of the ions and one atmospheric pressure (if there is gas) is measured with reference to normal Hydrogen electrode (used as cathode) the potential is orbitarly taken as ‘ZERO’. The normal hydrogen electrode also called as standard hydrogen electrode.

$$E = E^0 - RT/nF \log Oxi / red^n$$

At unit activity,

$$E = E^0 - RT/nF \log [Oxi / Oxi]$$

$$E = E^0 - RT/nF \log (1)$$

$$E = E^0 - RT/nF (0)$$

$$E = E^0$$

E^0 = Standard potential

II) Normal potential:-

The potential developed at the electrode it is dipped in the 1N solution is called Normal potential.

$$E = E^0 - RT/nF \log [Oxi/Red^n]$$

Here,

E = Normal potential

III) Formal potential:-

The potential developed at the electrode, the electrode is dipped on the formal solution (formula weight substance dissolved in water formal is molar).

Indicators:-

The substance which indicates the end point of particular reaction undergoing a colour change at end point is called indicator.

Types of indicators:-

I) Acid base indicator

II) Redox indicators

III) Complexo metric indicators

IV) Instrumental indicators

V) Self indicators

I) Acid base indicator:-

The substance which indicates the end point of acid- base reaction by undergoing a colour change at end point is called acid base indicator. Every indicator has its own pH range.

Indicators	pH range	Colour change
Methyl Orange	3.2- 4.7	Pink-Yellow
Methyl Red	4.4- 6.0	Red-Yellow
Phenol Red	6.8- 8.4	Yellow-Red
Phenolphthalein	8.3-10.0	Colourless-Pink

Methyl orange:-

It is a weak Organic base

$\text{Me OH} \rightarrow \text{Me}^+ + \text{OH}^-$

In basic medium-Yellow

In acidic medium-Pink

Phenolphthalein:-

It is a weak Organic acid.

$\text{H ph} \rightarrow \text{H}^+ + \text{ph}^-$

Selection of indicators:-

Titration	pH range end point	Indicator
Strong acid VS Strong base	3-10	Any indicator
Strong acid VS Weak base	3-7	Methyl Orange, Phenyl red, Phenol red
Weak acid VS Strong base	7-10	Phenol red, Phenolphthalein
Weak acid VS Weak base	No sharp change at end point	No indicator

II) Redox indicators:-

The substance which indicates the end point is Oxidant-Reductant reaction by undergoing a colour change the end point is called Oxidant- Reductant (or) Redox indicators.

Ex:-DPA, N- Phenyl Anthralenic acid, Ferroine, Starch, Di Methyl Ferroine.

III) Complexometric indicators:-

The substance which indicates the end point of metal complexing agent reactions (ligand) by undergoing a colour change the end point is called complexometric indicators.

Ex:-EBT, Solo chrome black-T, Murroxide.

IV) Instrumental indicators:-

They are two types.

I) Reference electrode- calomel electrode

II) Indicator electrode- Platinum electrode

V) Self indicators:-

Self indicators acts as a colour change at the end of the reaction majored coloured substance acts as a self indicators.

Ex:-$KMnO_4$, Ceric Sulphate

a) Inorganic systems:-

A) Mn (III):-

Properties:-

All Mn (III) salts are strong oxidizing agents.

The normal Redox potential value is +1.4V.

The general equation is

$$Mn^{+3}+1e^{-}\rightarrow Mn^{+2}$$

Hence trivalent Manganese is nearly as strong an oxidizing agent as $KMnO_4$.

The disadvantage of Mn (III) is stability of the solution enhanced by suitable complex agent.

Such as one complexing agent is Di Phosphate but the course of the above mentioned redox potential is demisted to +1.22V due to complex formation.

Preparation of standard solutions:-

These are two types:

I) The Mn (II) solution prepared by reducing a $KMnO_4$ solution with H_2O_2 in suitable conditions Mn^{+7} reduced to Mn^{+3}

II) It is prepared by Mn (II) oxidizing a solution with Bromated in the presence of Phosphoric Acid medium at elevated temperature. Care should be taken that Potassium ions are present in sufficient amount, after the Bromine has been removed by boiling an intensive volatile solution. Remains which is suitable eluated (Bi (V), Cr (VI) at higher temperature.

Standardization:-

The normality of Mn (III) solution is determined by potentio metric titrated with standard Fe (II) solution.

$$\text{Fe (II)} + \text{Cr (VI)} \rightarrow \text{Fe (III)} + \text{Cr (III)}$$

$$\text{Fe (II)} + \text{Mn (III)} \rightarrow \text{Fe (III)} + \text{Mn (II)}$$

To take 10mL Mn (III) solution is taken into a 100mL beaker and then added 5mL water and 5mL of 5N H_2SO_4 and 5mL H_3PO_4.Then ion is titrated with Fe (II) solution.

Applications:-

I) Determination of Iron Fe (II):-

To take 10mL of Fe (II) solution is taken into a 100mL beaker and then to this added 10mL H_2O and 5mL of 5N H_2SO_4 and 5mL of Phosphoric Acid. Then it is titrated with Mn (III) solution.

$$\text{Fe (II)} + \text{Mn (III)} \rightarrow \text{Fe (III)} + \text{Mn (II)}$$

II) Determination of Sn (II):-

To take 10mL of Sn (II) solution is taken into a 100mL beaker and then to this added 10mL of water and 5ml of 5N H_2SO_4 and 5mL of H_3PO_4.Then it is titrated with Mn (III) solution.

$$\text{Sn (II)} + \text{Mn (III)} \rightarrow \text{Sn (IV)} + \text{Mn (III)}$$

B) Mn (VII):-

Properties:-

KMnO4 is good colourful oxidizing agent.

The general equation is

$Mn^{+7} + 5e^{-} \rightarrow Mn^{+2}$

Here Mn^{+7} reduced to Mn^{+2} by gain of $5e^{-}$.

The redox potential value of Mn -1.5V

Preparation of $KMnO_4$ solution:-

Accurately weighed sufficient amount of $KMnO_4$ is taken into a one liter volumetric flask. Then it is dissolved in distilled water and shakes the solution.

Stability:-

The above $KMnO_4$ solution is transferred into amber colour bottle. After then to this CO_2 gas passed through the solution, then labeled the colour bottle and shake the solution, stand for few hours in a dark place. After then it is used for another analysis.

Standardization of $KMnO_4$:-

To take the 10mL $KMnO_4$ solution is taken into a 250mL conical flask. Then untreated Fe (II) is back titrated with $K_2Cr_2O_7$ solution.

$$Mn^{+7} + \text{excess of Fe (II)} \rightarrow Mn^{+2} + \text{Fe (III)}$$

$$\text{Untreated Fe (II)} + \text{Cr (VI)} \rightarrow \text{Fe (III)} + \text{Cr (III)}$$

Standardization of $KMnO_4$ by using Oxalic Acid:-

Accurately weighed 0.3g of Sodium Oxalate (or) Na_2CO_3 is taken into a beaker. Then to this added 240mL distilled water and 12.5mL of H_2SO_4. To take 10mL above solution is taken in to a conical flask. Then it is titrated with 0.02M $KMnO_4$ solution.

$$Mn^{+7} + C_2O_4^{-2} \rightarrow Mn^{+2} + CO_2 + H_2O$$

Indicators:-

i) Reference electrode-calomel electrode

ii) Platinum electrode-indicator electrode

iii) $KMnO_4$ it is a self indicator.

Applications:-

I) Determination of Hydrogen Peroxide (H_2O_2):-

Transfer 25mL of 6% of H_2O_2 solution by means of a burette into a 500mL volumetric flask and dilute with mark, shake thoroughly. The above solution pipette out 25mL solution taken into a conical flask and dilute with 250mL water and 20mL dilute with H_2SO_4.Finally it is titrated with standard $KMnO_4$ solution (0.02M).The end point is pink colour.

$$2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 2Mn^{+2} + 8H_2O + 5O_2$$

II) Determination of Nitrite (NO_2^-):-

Accurately weighed sufficient amount of Potassium Nitrite taken into a 250mL volumetric flask. It is dissolved in water up to the mark. Then to take 10mL pipette out the above solution taken into a conical flask. Then to this added 20ml distilled water and 10mL H_2SO_4.Then it is titrated with standard 0.02M $KMnO_4$ solution.

$$2MnO_4^- + 5NO_2^- + 6H^+ \rightarrow 2Mn^{+2} + 5NO_3^- + 3H_2O$$

III) Determination of Per Sulphate ($S_2O_8^{2-}$):-

Alkali per Sulphate can readily be evaluated by adding excess of acidified Fe (II) salt solution and determining the untreated Fe (II) back titrated with standard $KMnO_4$.

$$S_2O_8^{-2} + \text{excess Fe (II)} + H^+ \rightarrow HSO_4^- + \text{Fe (III)}$$

$$\text{Untreated Fe (II)} + Mn^{+7} \rightarrow \text{Fe (III)} + Mn^{+2}$$

IV) Determination of Sn (II):-

Accurately weighed sufficient amount of Sn (II) is taken into a250mL volumetric flask. Then it is diluted with water up to the mark. Then to take 10mL of above solution pipette out in a 250mL conical flask. After then to this added 10mL water then it is titrated with standard $KMnO_4$.

$$Mn^{+7}+SnCl_2{}^{+2}+H^{+}\rightarrow Mn^{+2}+Sn^{+4}+HCL$$

v) Applications are writing with oxidant like Cr (VI), V (V), and Ti (IV) with reductant like Fe (II).

C) Ce (IV):-

Properties:-

Cerium is a powerful oxidizing agent.

It self reduced and other substance will be oxidized.

It has an intensive yellow colour.

The redox potential value is 0.5- 4m H_2SO_4 at 25^0C is 1.43±0.05V.

Preparation of 0.1M Ce (IV) Sulphate:-

Accurately weighed 35-36g of pure ceric sulphate is taken into a 500mL beaker. Then to this added 56mL of 1:1 H_2SO_4 by water and stir with frequent additions of water and gentle warming, until the salt is dissolved transfer to a one liter glass stopped graduated flask and then diluted up to the mark with distilled water.

Stability:-

The above Ceric sulphate solution transferred into an amber colour bottle. Then CO_2 gas is passed through the solution, the labeled the bottle and shake the solution and for few hours in dark place. After then it is used for another analysis.

Indicators:-

I) N-Phenyl Anthracitic acid

II) Ferroine (1, 10-Phenathraline Fe (II))

III) 1, 5, 6 Di Methyl Ferroine

Standardization of Ceric Sulphate by using Sodium Oxalate:-

Accurately weighed 0.2g of Sodium Oxalate is taken into a 250mL conical flask. Then to this added 25-30mL 1M H_2SO_4 and heat the solution and then to this added excess known amount of Ce (IV) solution. The untreated Ce (IV) Sulphate is backing titrated 0.1M Fe (II) solution by using ferroine as an indicator.

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

$$\text{Sodium oxalate + known excess Ce (IV) +untreated Ce (IV)} \rightarrow \text{Fe (II).}$$

Applications:-

I) Determination of Iron:-

To take 10mL of Ce (IV) solution is taken into a conical flask and then to this added 10mL of distilled water and then 5mL of 5N H_2SO_4 and 3mL of H_3PO_4.then it is titrated with standard Fe (II) solution.

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

II) Determination of Chromium:-

To take sufficient amount of Chromium solution is taken into a volumetric flask. Then to take 10mL of Chromium solution in 250mL conical flask. Then to this added excess amount of Fe (II), then to this added distilled water and then this solution is titrated with Ce (IV) solution by using ferroine as aindicator.

$$\text{Cr}^{+6} + \text{Excess of Fe (II)} \rightarrow \text{Untreated Fe (II)} \rightarrow \text{Ce (IV)}$$

$$\text{Cr}^{+6} + \text{Fe (II)} \rightarrow \text{Cr}^{+3} + \text{Fe (III)}$$

$$\text{Untreated Fe (II)} + \text{Ce (IV)} \rightarrow \text{Fe (III)} + \text{Ce (III)}$$

III) Determination of Sn (II):-

To take 10mL of Sn(II) solution is taken into a conical flask and then to this added excess of known Ce (IV) and water and then untreated Ce (IV) is back titrated with standard Fe(II) solution by using ferroine as a indicator.

$$\text{Sn}^{+2} + \text{Excess of known Ce (IV)} \rightarrow \text{Untreated Ce (IV)} \rightarrow \text{Fe (II)}$$

$$\text{Sn (II)} + \text{Excess of Ce (IV)} \rightarrow \text{Sn (IV)} + \text{Ce (IV)}$$

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

IV) Determination of Cu^{+2}:-

To take 10mL of Copper solution is taken into a conical flask and then to this added excess amount of Fe (II) the untreated Fe (II) present and then to this added distilled water and then this titrated with Cerium (IV).

$$\text{Cu+2} + \text{Fe (II)} \rightarrow \text{Cu (I)} + \text{Fe (III)}$$

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

D) Cr (VI):-

Properties:-

Potassium Di Chromate is a not such as a powerful oxidizing agent then compare with Potassium Permanganate, But it has several advantages over the later substance.

It can be obtained; it is stable up to fusion point.

It is excellent primary standard.

The Redox potential value is -0.74V

$$Cr (VI) \rightarrow Cr (III)$$

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

Preparation of 0.02M of Di Chromate solution:-

Accurately weight sufficient amount of Di Chromate is taken in to a one liter volumetric flask. Then it is dissolved in distilled water up to the mark.

Stability:-

The above solution is transferred in to an amber colour bottle. Then CO_2 gas passed, and it acts as a maintained acidic medium & close the bottle & shakes well & stands for few hours. This is used for another Analysis.

Standardization of dichromate:-

Accurately weight sufficient amount of Di Chromate solution is taken into a 250 ml volumetric flask. Then it is dissolved in water. To take above 10 ml solution in to a 250 ml conical flask. Then to this added 20 ml distilled water and 5 ml H_2SO_4 & 3ml H_3PO_4 .Then it is titrated with standard Fe (II) solution by using DPA (or) N-Phenyl Anthracitic acid.

$$Cr^{+6} + Fe (II) + H^+ \rightarrow Cr^{+3} + Fe (III) + H_2O.$$

Applications:-

I) Determination of Fe (III) Ferric Iron:-

To take 10 ml Fe (III) solution is taken into a 250 ml conical flask. Then to this added 10 ml of Oxalic Acid & 10 ml distilled water. It is placed at sunlight. After few min the solution is titrated with standard Di Chromate in the present of acidic medium (phosphoric acid) by using DPA indicator.

$$Fe (II) + Cr_2O_7^{-2} \rightarrow Fe (III) + Cr (III) + H_2O$$

$$Fe (III) + \text{Oxalic acid} \rightarrow \text{(Fe-Oxalate) complex} \xrightarrow{\text{Sunlight}} Fe (II) + CO_2 + H_2O$$

II) Determination of Cr (III):-

Cr (III) salts are oxidized to Di Chromate by boiling with excess of a Per Sulphate solution in the presence of a little amount of $AgNO_3$ (catalyst). The excess per sulphate remaining after oxidation is completed distorted by boiling the solution for a short time. The resulting solution is determined by the addition of excess amount of standard 0.02M $K_2Cr_2O_7$ solution.

$$2Cr^{+3} + 3S_2O_8^{-2} + 7H_2o \rightarrow Cr_2O_7^{-2} + 6HSO_4^- + 8H^+$$

$$S_2O_8^{-2} + H_2O \rightarrow HSO_4^- + O_2$$

$$Cr (III) + Fe (II) \rightarrow Cr^{+3} + Fe^{+3} + \text{untreated Fe (II)}$$

$$Fe (II) \rightarrow \text{Titrated standard } K_2Cr_2O_7$$

$$Fe (II) + Cr_2O^{-2} + H^+ \rightarrow Fe^{+3} + Cr^{+3} + H_2O$$

Procedure:-

To take 10 ml Cr (III) solution is taken in to a250 volumetric flask. Then to this added 20 ml $S_2O_3^{-2}$ & 5 ml $AgNO_3$ & 20 ml distilled water. This solution is boiled. After then to this added excess amount of 25 ml Fe (II) solution & 5 ml H_2SO_4 & 5 ml H_3PO_4. Then it is back titration with $K_2Cr_2O_7$ by using DPA as an indicator.

III) Determination of Chlorate (ClO_3^-):-

Chlorate ion is reduced by warming with excess of Fe (II) in the presence of H_2SO_4.

$$ClO_3^- + Fe\ (II) + 6H^+ \rightarrow CL^- + 6Fe^{+3} + 3H_2O$$

The excess of Fe (II) ion is determined by titrate with standard Di Chromate solution.

$$Fe\ (II) + Cr_2O_7^{-2} + H^+ \rightarrow Fe\ (III) + 2Cr^+3 + H_2O$$

Procedure:-

To take 10 ml of Chlorate solution is taken into a250 ml conical flask. Then to this added 20 ml distilled water & it is titrate with $K_2Cr_2O_7$ by using DPA as a indicator

IV) Determination of Vanadium:-

V (V) present in the sample solution it is reduced by V (IV) the by adding of excess amount of Fe (II). The untreated Fe (II) is back titration with standard $K_2Cr_2O_7$ solution.

To take 10 ml of Vanadium solution is taken into a 250 ml conical flask. Then to this added 10 ml Fe (II) solution & H_2SO_4 & 10 ml distilled water. The untreated Fe (II) is titrated with $K_2Cr_2O_7$ with by using DPA as an indicator

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

$$Fe\ (II) + Cr\ (VI) \rightarrow Fe\ (III) + Cr^{+3}$$

E) V (V):-

Properties:-

Vanadium is a power full oxidizing agent. It is itself reducing agent other substance will be oxidized.

The Redox potential value -0.255V-0.999V

$$V^{+5} + e^- \rightarrow V^{+4}$$

$$VO_4^{-3} + e^- \rightarrow VO^{+2} + H_2O$$

Preparation of ammonium MetaVanadate:-

Accurately weight sufficient amount of Vanadium is taken in to a one liter volumetric flask. Then it is dissolved in to a hot water up to the mark.

Stability:-

The above solution is transferred in to amber colour bottle. Then to this CO_2 gas passed through it. Then it at as an acidic medium and the close the bottle state well and stand for few hrs. This is used for another analysis.

Standardization: -

Instrument: -Platinum electrode and calomel electrode.

Indicator:-DPA Indicator

Required solutions:-

I) Ammonium MetaVanadate

II) Mohr's salt

III) Dichromate

Standardization of vanadium:-

Procedure: -

To take 10ml Vanadium solution is taken in to a 250ml conical flask. Then to this added 20ml standard Fe (II) solution and 10ml water and 5mL H_2SO_4 and 3mL $H_3PO_4$and 2(or) 3 drops DPA indictor. Then it is titrated with standard dichromate.

$$\text{V (V)} + \text{Fe (II)} \rightarrow \text{V (IV)} + \text{Fe (III)}$$

$$\text{Fe (II)} + \text{Cr (VI)} \rightarrow \text{Fe (III)} + \text{Cr (III)}$$

Application:-

I) Determination of Cerium:-

Cerium present in the sample Ce (IV) is reduced to Ce (III) by the adding of excess iron is back titrated with standard Vanadium solution by Potentio metric titration.

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

$$\text{Fe (II)} + \text{V (V)} \rightarrow \text{Fe (III)} + \text{V (V)}$$

Procedure:-

To take 10ml of Cerium solution is taken in to a conical flask. Then to this added 20ml of distilled water and Fe (II). The untreated Fe (II) is titrated with Vanadium by using DPA indicator, by using calomel electrode.

II) Determination of Titanium:-

Titanium present in the sample Ti (IV) is reduced to Ti (III) by the adding of excess Fe (II). The untreated Fe (II) is back titration.

$$\text{Ti}^{+4} + \text{Fe (II)} \rightarrow \text{Fe (III)} + \text{Ti (III)}$$

$$\text{Fe (II)} + \text{V (V)} \rightarrow \text{Fe (III)} + \text{V (V)}$$

Procedure:-

To take 10ml of Titanium solution is taken in to a conical flask. Then to this added 20ml of distilled water and Fe (II) add solution. The untreated Fe (II) is back titrated with standard solution by using DPA indicator by using calomel electrode.

III) Determination of Chromium:-

Chromium present in the sample Cr (III) is reduced to Cr (VI) by the adding excess of Fe (II). The untreated Fe (II) is back titration with standard Vanadate solution by potentio metric titration.

$$\text{Cr (VI)} + \text{Fe (II)} \rightarrow \text{Cr (III)} + \text{Fe (III)}$$

$$\text{Fe (II)} + \text{V (V)} \rightarrow \text{Fe (III)} + \text{V (V)}$$

Procedure:-

To take 10ml Chromium solution is taken in to a conical flask. Then to this added 20ml of distilled water and Fe (II) vanadate solution by using DPA indicator by using calomel electrode.

IV) Determination of manganese:-

Manganese present in the sample Mn (VII) is reduced to Mn (II) by adding excess of Fe (II). The untreated Fe (II) is back titrated with standard Vanadate solution by potentiometric titration.

$\text{Mn (VII)} + \text{Fe (II)} \rightarrow \text{Mn (II)} + \text{Fe (III)}$

$\text{Fe (II)} + \text{V (V)} \rightarrow \text{Fe (III)} + \text{V (IV)}$

Procedure:-

To take 10ml of Manganese solution is taken conical flask. Then to this added 20ml of distilled water and Fe (II) solution is added. Then untreated with Fe (II) is back titration with vanadate solution by using DPA indication. This is using the calamol electrode.

F) Per Iodate [IO_4^-]:-

Properties:-

Per iodate is a powerful oxidizing agent.

It is itself reduced other substance will be oxidized.

Per iodide are also reduced by Sulphorous acid and therefore be similarly determine iodate procedure.

$$IO_4^- + 2H^+ + 2e^- \rightarrow IO_3^- + H_2O$$

The Redox potential valve is 1N H_2SO_4 is 1.375V.

Preparation of per iodide:-

Aqueous solution of ortho periodic acid, 3^0- Sodium salt of ortho periodic acid and of the Potassium (or) Sodium salts of Meta Periodic acid are generally used as solutions.

The solution is prepared by dissolving the commercially available substance. If the solution is not clear enough it is set aside for 24 hours then filter. The solution stable at normal temperature, at boiling temperature there one less stable.

Stability:-

It is stable at room temperature.

Indicator:-1- Naphthalene Black 12B (Green to Pink)

2- Xylidine.

Standardization:-

The standardization is done by the iodine method. In buffered alkaline solution per iodide reduced to iodate.

$$IO_4^- + H^+ \rightarrow IO_3^- + H_2O$$

Standardization of IO_4^- by using Ar (III) acid:-

Per iodide is reduced to iodate by the adding of sulphorous aid. Then it is placed kept inside. The above solution is standard Ar (III) oxide.

To take 10 ml of Arsenic (III) solution is taken in to a 250 ml conical flask and then to this added HCL & 250ml of water & cool at temperature. This is titrating with standard per Iodate solution (or) Iodate solution.

$$IO_4^- + H^+ \rightarrow IO_3^-$$

The above procedure follows below equation

$$IO_3^- + H_3AsO_3 + H^+ \rightarrow I^- + H_3AsO_4 + H_2O$$

Applications:-

I) Determination of Hydrazine:-

Hydrazine reacts with KIO_3^- under the usual on rules conditions. This equation

$$IO_3^- N_2H_4 + 2H^+ + 2Cl \rightarrow ICL + N_2 + 3H_2O$$

Procedure:-

Accurately weight 0.1g Hydrazinium Sulphate is taken in to a 250 ml reagent bottle & then to this added 30ml of concentration of HCL & 20ml distilled water & 5ml chloroform. Then the solution is titrated with 0.02m KIO_3^- by number of addition the KIO_3^-solution. The organic layer is decolorised

II) Determination of Mercury:-

Mercury it is precipitate as Mercury (I) Chloride, it is react with standard KIO_3^- solution.

$$IO_3^- 2Hg_2Cl_2 + 6H^+ + 13Cl \rightarrow ICL + (HgCl_4)^{-2} + 3H_2O$$

Procedure:-

Accurately weight 2.2g of Hg (II) Chloride dissolve in 100ml water in a graduated flask, shake well & 25ml of solution is taken in to a conical flask. Then to this added 25ml water & 2ml of ml HCL& excess 50% of phosphorous (III) acid solution. Stand for few hours & filter the precipitate Hg (I) through a filter paper. Wash the precipitation with cold water. Then it is placed at a 250ml reagent bottle. Then to this added 20ml concentration HCL& 20ml distilled water & 5ml CCL_4 chloroform. Then it is titrated with standard KIO_3^- solution.

$$HgCl_2+H_3PO_3+H_2O\rightarrow HgCl_2+2HCL+H_3PO_3$$

G) Iodate (IO_3^-):-

Properties:-

Potassium iodate is a powerful oxidizing agent.

The reaction between Potassium iodate (KIO_3^-) & reducing agent such as iodide (I^-) ion (or) Arsenic (III) oxide in solution of moderate acidity (0.1-2M HCL)

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

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

The Redox potential valve is 1.23V.

$$IO_3^-+I^-+6H^+\rightarrow I_2^++H_2O$$

Preparation of 0.025M Potassium iodide (KIO_3^-):-

Accurately weight 5.350g KIO_3^- in to a one liter flask. Then it is dissolved in distilled water in the presence of acetic medium up to the mark.

Indicators:-

I) Naphthalene black 12.8 (Green to Paint pink).

II) Xylidine – ponceau (Orange to colourless)

III) Starch

Standardization of KIO_3^- by using Arsenic (III) Oxide:-

Accurately weight 1.1g of Arsenic (III) oxidizing sample is dissolved in a 10% NaOH solution make up to 250 ml volumetric. To take above 25ml solution is taken into a 250 ml conical flask. Then to this added 25ml distilled water and

60ml of HL& 5ml 0f CCL_4 (or) Chloroform. This solution is cooled at a room temperature. This solution is titrated with 0.025 M KIO_3^- solutions. The colour change is purple to pale yellow.

$$2IO_3^-+2H_3AsO_3+2H^++Cl^-\rightarrow ICL+2H_3AsO_4+H_2O$$

$$IO_3^-+I^-\rightarrow I_2$$

First it is strongly from coloured with Iodine becomes pale brown. This solution is vigorously shake & the organic solvent layer acquires the purple colour due to iodine continue to this add small volumes of iodine solution & then shaking vigorously. After each addition until the organic layer is only very faintly violet. Continue this addition of drop wise with shaking after each drop until the solvent losses the layer of violet& has only a very pale yellow colour. It is iodine chloride.

Applications:-

I) Determination of Hydrazine:-

Hydrazine reacts with KIO_3^- under the usual on rules condition. In this equation.

$$IO_3^-N_2H_4+2H^++Cl^-\rightarrow ICl+N_2+3H_2O$$

Procedure:-

Accurately weight 0.1g of Hydraziniun Sulphute is taken in to a 250ml reagent bottle& to this add 30ml of concentration of HCL & 20ml distilled water & 5ml of chloroform. Then the solution is titrated with 0.02m KIO_3^- by number of additions to the KIO_3^- organic layer is decolorised.

II) Determination of Mercury;-

Mercury it is precipitate as mercury+1-chloride& later it is reacting with standard KIO_3 solution.

$$IO_3^-2Hg_2Cl_2+6H^++13Cl\rightarrow Cl+4(HgCl_4)^2+3H_2O$$

Hg (II) is converted to Hg (I) buy the adding of H_3PO_4.

Procedure:-

Accurately weight 2.2g of Hg (I) chloride dissolve in 100ml water in a graduated flask. Shake well & transferred 25mkl of solution is taken in to a conical flask. Then to this added 25 ml water & 2ml of 1m HL& excess 50% phosphorous (III) acid solution & stand for few hours & filter the precipitate Hg (I) chloride through a filter paper. Precipitate is washing with cold water then it is placed at a 250ml reagent bottle. Then to this added 20 ml on HCL & 20ml distilled water& 5ml of CCL_4 (or) chloroform. Then the solution is titrated with KIO_3^- solution.

$$HgCl_2+H_3PO_3+H_2O\rightarrow HgCl_2+2HCl+H_3PO_4$$

b) Organic system:-

Chloramine-T:-

The sodium salt of P-Toluene Sulpho Chloramide ($CH_3C_6H_4SO_2N$ NaCl $3H_2O$) know as Chloramine-T it`s act as an Oxidant in Alkali as well as acid solution.

In aqueous solution Chloramine-T consider too according to the following equation.

The potential of Chloramine is 1N H_2SO_4 is 1.52V, in neutral solution is 0.90V.

Standard Solution:-

The standard solution is prepared by dissolved the pure substance. If the Chloramines-T is impure, it has to be re crystallized from hot water& dried & over concentrated H_2SO_4. The aqueous solution react alkaline & shows every point.

Stability:-

Aqueous Chloramine-T solution is very stable. It is stored in dark bottles. They do not change their true titer for several months& boiling for several hours& likewise does not change their true titer.

Standardization:-

The solution is standardized Iodo metrically (or) by titrating with is an Arsenate solution.

Procedure:-

Add 25ml of 0.5N KIO_3^-& 25ml of HCL& 30ml chloramines is 0.1N solution is titrated with $Na_2S_2O_3$(Hypo0.01N)

$$\text{Chloramine-T}+KI \rightarrow I_2$$

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

(Or)

25mL of 0.1N Arsenate solution in the presence of $NaHCO_3$ and then to this added 0.5g of Potassium Iodide,1mL starch is taken into a conical flask. Then this solution is titrated with Chloramine-T

Indicator:-Starch, Methyl red, Dye stuff

Hydrolysis:-

$$\text{P- Toluene Sulpho Chloramide} + H^+ \rightarrow C_6H_6\text{-}CH_3\text{-}SO_2\ NH\text{-}Na^+ + HOCl$$

$$HOCl + NaOH \rightarrow NaClO + H_2O$$

$$\text{Chloramine-T}+KI \rightarrow I_2$$

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

Applications:-

I) Determination of Arsenium solution:-

To take 25ml of 0.1N Arsenate solution in the presence of $NaHCO_3$ & then to this added 0.5g KIO_3^- & 1ml starch as an indicator. Then the solution is titrated with Chloramine-T.

$$H_3AsO_3+ \text{Chloramine-T} + H_2O \rightarrow H_3ASO_4+NaCl+NH_2\text{-}SO_2C_6H_6\text{-}CH_3$$

II) Determination of Sn (II):-

To take 25mL of 0.1N Sn (II) solution in the presence of $NaHCO_3$& added 0.5g of KIO_3^-& 1ml of starch. Then the solution is titrated with Chloramine-T.

$$Sn^{+2}+\text{Chloramine-T}+ H_2O \rightarrow SnO_2+2NaCl+NH_2\text{-}SO_2C_6H_6\text{-}CH_3$$

UNIT-IV

ORGANIC FUNCTIONAL GROUP ANALYSIS

Classification of functional group with suitable examples:

i) Qualitative analysis:-

What are elements present in the sample (or) which type of compound present in the sample is called Qualitative analysis?

ii) Quantitative analysis:-

How much amount of the sample (or) Substance present in the sample is called Quantitative analysis**.**

iii) Functional group:-

This tells about the nature of the substance, the functional group broadly classified into 3 types.

a) Functional groups imparting acidic nature

b) Functional groups imparting basic nature

c) Functional groups which impart neither acidic nor basic nature

a) Functional groups imparting acidic nature:-

Ex: - -COOH (Carboxylic Acid),-SO_3H (Sulphonic Acid), C_6H_6-OH (Phenol Hydroxyl group), Diols, R-S-H (Thiol).

b) Functional groups imparting basic nature:-

i) Aliphatic Amines: -Ex: - R-NH_2, R_2-NH, R_3-N.

ii) Aromatic amines: - Ex: - Ar-NH_2, Ar-NHR, Ar-NR_2

iii) Hydrazine: - Ex: - -NH_2-NH_2

iv) Hydrazine derivatives:-Ex: - NH_2-NHR, NHR-NR_2, NH_2-NR_2, NR_2-NR_2

c) Functional groups which impart neither acidic nor basic nature:-

Ex: - Carbonyl group, Acetylenes, Ethoxy group, Esters, Ethers, Nitro group.

a) Functional groups imparting acidic nature:-

i) Thiol:-

These are determined by two methods:

1) Volumetric method:-

Principle:-

Thiol sample is reacted with Iodine, then to form Di thiols and then to this added excess amount of Iodine solution. Then excess of Iodine is liberated, and then liberated Iodine is titrated with Hypo ($Na_2S_2O_3$) by using starch as an indicator. Then solution colour change to blue to colourless is the end point.

$$2RSH + I_2 \rightarrow RSSR + 2HI$$

Chemicals required: - Sample, I_2, Ethanol, and $Na_2S_2O_3$, Starch.

Procedure:-

To take 0.2-0.6g of sample is taken into a 250mL conical flask. After then to this added 50mL of I_2 (0.1N) solution and then shake the solution for 5min.After then to this added 20mL of Ethyl Alcohol and shake well for 10-15min, then this solution is standard solution. The standard solution is untreated I_2 solution. Then untreated I_2 is titrated with Hypo ($Na_2S_2O_3$) by using starch as an indicator. This solution colour change Blue to colourless.

$$\% \text{ Thiols} = \frac{(V_1-V_2) \times N \times M \times 100}{1000 \times W}$$

Here,

V_1 = Volume of Hypo ($Na_2S_2O_3$) consume during the blank titration
V_2 = Volume of Hypo ($Na_2S_2O_3$) consume during the sample titration
N = Normality of Hypo ($Na_2S_2O_3$)
W = Weight of the sample
M = Molecular weight of the sample

2) Argentometric method:-

Principle:-

To take required quantity of Thiol sample is taken into a 250mL conical flask. After then to this added excess of $AgNO_3$ solution. Then to form R-S-Ag and HNO_3.Then the excess of$AgNO_3$ solution is titrated with untreated NH_4SCN by using ferric alum as an indicator.

$$2RSH + \text{Excess}AgNO_3 \rightarrow R\text{-}S\text{-}Ag + HNO_3$$

Chemicals required: - Sample, $AgNO_3$, NH_4SCN, and Ferric alum (Ferric Ammonium Sulphate), Methanol.

Preparation of $AgNO_3$:-

Weighed out required quantity of $AgNO_3$ and it is dissolved in distilled water and make up to the mark**.**

Preparation of NH_4SCN:-

Weighed out required quantity of NH_4SCN is taken into a 250mL volumetric flask. Then it is dissolved water and make up to the make.

Preparation of Ferric alum (Ferric Ammonium Sulphate):-

To take the 4g of Ferric alum in 10mL of Nitric acid (N), boiled the solution then to remove the Oxides of Nitrogen, then it is cooled and dilute with 30mL of distilled water.

Procedure:-

To take 1 (or) 2g of Thiol sample is dissolved in 100mL of Benzene solution. From the above solution we take 10mL and then to this added 45mL of $AgNO_3$ solution. Shake the solution thoroughly for 5min and then to this added few ml anhydrous methanol, shake the solution and then settle for 10-15min. Then the untreated $AgNO_3$ solution is titrated with standard NH_4SCN by using Ferric alum as indicator.

$$\% \text{ Thiol} = \frac{V \times N \times 33.07 \times 100}{1000 \times W}$$

Here,

V = Volume of $AgNO_3$
N = Normality of $AgNO_3$
W = Weight of the sample

ii) Enediol:-

Principle:-

The determination of Diol sample solution and then to this added known excess amount of Potassium per Iodide solution. Then the untreated Potassium Per Iodate gives Iodine and Iodic acid by adding of 20% of KI belong the 6N H_2SO_4.Then Iodine is liberated. Then the liberated I_2 is titrated with Hypo ($Na_2S_2O_3$) by using starch as indicator.

Chemicals required: - Sample, KIO_4, 20% KI, 6N H_2SO_4, Hypo ($Na_2S_2O_3$), Starch.

Preparation of Hypo (Sodium Thio Sulphate $Na_2S_2O_3$):-

Dissolve 3g of Sodium Thio Sulphate is 500mL of boiled water and cooled and make up to the mark with distilled water.

Preparation of Potassium Iodide (KI):-

To take 40g of Potassium Iodide is dissolved in 200mL distilled water.

Preparation of per Iodide:-

Weighed out required quantity of per Iodide is making up to the mark with distilled water.

Procedure:-

To take 0.2-0.6g sample is taken into a250mL volumetric flask and make up to the mark with distilled water.

To take above the solution and then to this added 50mL of Potassium per Iodide solution. Then this solution is shaking thoroughly for 10-15min. After then to this added 20mL of 20% KI and few ml of 6N H_2SO_4 and this solution is stand for 30min.Then I_2 is liberated. Then the liberated Iodine is titrated with standard Hypo ($Na_2S_2O_3$) by using starch as indicator.

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

$$\% \text{ Diols} = \frac{V \times N \times M \times 100}{1000 \times W}$$

Here,
V = Volume of hypo consumed by during the sample titration
M = Molecular weight of the sample
N = Normality of the Hypo ($Na_2S_2O_3$)
W = Weight of the sample

iii) Phenolic Hydroxyl:-

Determination of Phenols:-

Principle:-

To take the Phenol and then it is treated with excess amount of water. Then to form a Tri Bromo Phenol. Then excess amount of Bromine is titrated with KI and then I_2 is liberated .Then the liberated Iodine is titrated with Hypo ($Na_2S_2O_3$) by using starch as an indicator**.**

Chemical required: - Sample, Bromine water, 20% KI, $Na_2S_2O_3$, and Starch.

Preparation of Bromination mixture:-

Dissolve 1.5g of Potassium Bromate ($KBrO_3$) and 20g of Potassium Bromite in distilled water and make up to the mark with 250mL volumetric flask.

Preparation of Potassium Iodide (KI):-

To take 40g of Potassium Iodide is dissolved in 200mL distilled water.

Preparation of Hypo (Sodium Thio Sulphate $Na_2S_2O_3$):-

Dissolve 3g of Sodium Thio Sulphate is 500mL of boiled water and cooled and make up to the mark with distilled water.

Procedure:-

To take 0.5g of sample is taken and it is dissolved in 10% of NaOH and make up to the mark with 250mL volumetric flask with distilled water.

To take above the solution and this solution is 25mL of solution is taken in to a conical flask. After then to this added known amount of Brominating mixture and 25mL of distilled water and 5mL of concentration of HCL and this solution is stand for 20min. then to form a Tri Bromo Phenol. After then to this added 10mL of 20% of KI and this solution is stand for 10min.After then I_2 is liberated, the liberated Iodine is titrated with Hypo by using starch as indicator.

$$\%\text{Phenols} = \frac{(V_2 - V_1) \times N \times M \times 100}{2000 \times W \times Z}$$

Here,

V_2 = Volume of Hypo ($Na_2S_2O_3$) consumed by during blank titration
V_1 = Volume of Hypo ($Na_2S_2O_3$) consumed by during sample titration
N = Normality of Hypo ($Na_2S_2O_3$)
W = Weight of the sample
M = Molecular weight of the sample
Z= Number of Bromines substituted in phenols (or) Number of moles of Bromine used for Bromination.

b) Functional groups imparting basic nature:-

Difference between Aliphatic and Aromatic Amines:

Ignition test:-

Place the given substance on flame with help of Nickel spatula.

Here sooty flame is observed. Then it is called Aromatic compounds.

Here non sooty flame is observed. Then it is called Aliphatic Amines.

Test for primary amines:-

Carbyl amines test:-

A few grams of Amine is taken into a test tube and then to this added2mL of Ethanol and few ml of $CHCl_3$ and NaOH solution. Heat the solution gently, and then unpleasant order is observed then to form an Isocyanides.

Azo dye test:-

Dissolve 3mL of Aniline in 3mL of concentration of HCL and cool the solution up to $0+5^0$C add a cooled solution of one gram of $NaNO_2$ in 5mL water slowly adding and with stirring, after this solution is standing for 3-4min. The result in Dye azonium solution and then to this added cooled solution of 0.4g of β-Napthol in 4mL of 5% NaOH slowly and with stirring, then to form a Orange- Red dye is formed. It indicates primary Amines.

Test for Secondary Amines:-

Dissolve 1mL of Aniline in 3mL of concentration of HCL and cool the solution up to $0\text{-}5^0$C add a cooled solution of one gram of $NaNO_2$ in 5mL water slowly adding and with stirring, after this solution is standing for 3-4min. the result in dye azonium solution and then to this added cooled solution of 0.4g of β-Napthol in 4mL of 5% NaOH slowly and with stirring, then do not form a Orange- Red dye. It doesn't which represent the secondary Amines.

Tests for Tertiary Amines:-

Reaction with Nitrous acid:-

Dissolve 1g of Amine in 10mL of diluted HCL, this solution is cooled up to $0\text{-}5^0$C and then to this added 0-7g of $NaNO_2$ in 4mL of water with stirring, after 20-30min, filter of the yellow hydrochloride is added and NaOH solution is added. Then we get a green crystal. It indicates the 3^0 amines.

1) Determination of Aliphatic and Aromatic Primary, Secondary, and Tertiary Amines:-

Principle:-

Amines give a coloured compound (Tri Bromo Aniline) by the addition of brominating mixture**.**

When the sample is reacted with excess amount of brominating mixture and it gives a Tri Bromo Aniline. The untreated Bromine is treated with Potassium Iodide. The liberated Iodine is titrated with Hypo ($Na_2S_2O_3$) by using starch as an indicator.

Chemicals required:-Sample, Brominating mixture, 20% KI, $Na_2S_2O_3$, and Starch.

Preparation of Brominating mixture:-

Dissolve 1.5g of Potassium Bromate ($KBrO_3$) and 20g of Potassium Bromite (KBr) in distilled water and make up to the mark with 250mL volumetric flask.

Preparation of Potassium Iodide (KI):-

To take 40g of Potassium Iodide is dissolved in 200mL distilled water.

Preparation of Hypo (Sodium Thio Sulphate $Na_2S_2O_3$):-

Dissolve 3g of Sodium Thio Sulphate is 500mL of boiled water and cooled and make up to the mark with distilled water.

Procedure:-

To take the 25mL of sample solution is taken into a round bottom flask (RBF). After then to this added 20mL of brominating mixture in the presence of 10mL of concentration of HCL. After then to this added 10mL of 20% of KI solution. Then I_2 is liberated. Then liberated Iodine is titrated with Hypo ($Na_2S_2O_3$) by using starch as an indicator.

Total concentration of Amines (primary, secondary, tertiary):-

In the determination of Amines initially to must prepare a solvent mixture (Ethylene, Glycol, and Isopropyl).

To take 0.02g of sample is taken into a round bottom flask. After then to this added 50mL of solvent mixture and this solution is shaking thoroughly for 5min. Then this solution is titrated with 1N HCL solution.

$$\text{Concentration of Amines} = \frac{\text{Volume of HCL X Normality of HCL X 100}}{\text{Total weight of the sample}}$$

Concentration of secondary & tertiary Amines:-

To take required quantity of sample is taken into a round bottom flask. After then to this added 5mL of salicylaldehyde and heat for few min. After then to this added 50mL of solvent mixture. Then this solution is titrated with 1N HCL solution.

$$\text{Concentration of secondary \& tertiary Amines} = \frac{\text{Volume of HCL X Normality of HCL X 100}}{\text{Total weight of the sample}}$$

Concentration of tertiary Amines:-

To take require quantity of sample is taken into round bottom flask. After then to this added 50mL of solvent mixture and then to this added 10mL of acetic anhydride. Then this solution is titrated with 1N HCL solution.

$$\text{Concentration of tertiary Amines} = \frac{\text{Volume of HCL X Normality of HCL X 100}}{\text{Total weight of the sample}}$$

Concentration of primary Amines:-

Concentration of primary Amines = Concentration of (primary+ secondary+ tertiary) - Concentration of (2^0+3^0 Amines)

Concentration of secondary Amines:-

Concentration of secondary Amines = Concentration of (secondary+ tertiary) - Concentration of (3^0 Amines)

2) Determination of hydrazine derivatives:-

Principle:-

To take the Hydrazine sample is taken into a conical flask. After then to this added excess amount of reducing agent Titanium Sulphate [$Ti_2(SO_4)_3$]. The untreated [$Ti_2(SO_4)_3$] is titrated with standard Ferric Ammonium Sulphate by using Ammonium Thio cyanide as an indicator.

$$R\text{-}NH\text{-}NHR + 6Ti^{+3} + 6H^{+} \rightarrow R\text{-}NH_2 + 6Ti^{+4} + H_2O$$

Chemicals required: - Sample, [$Ti_2 (SO_4)_3$], Ammonium ThioCyanide, Ferric Ammonium Sulphate (Ferric alum), and HF.

Procedure:-

To take sufficient amount of sample is taken into a 500mL round bottom flask. Then it is dissolved in water but if it is insoluble in water. It is dissolved in Acetic acid. After then CO_2 is passed through the flask and then maintain the inert atmosphere in the flask. After then to remove the Oxygen from the round bottom flask. After then to this added 25mL of Titanium Sulphate and 30mL of concentration of HCL and 2mL of HF solution is added. Then this solution is boiled for 5min. After then this solution is cooled and then titrated with standard Ferric alum by using Ammonium thio cyanide as an indicator.

$$\% \text{ Hydrazine} = \frac{(V_1-V_2) \text{ X N X W}}{1000 \text{ X A}}$$

Here,

V_1 = Volume of Ferric alum consumed by during the blank titration
V_2 = Volume of ferric alum consumed by during the sample titration
N = Normality of Ferric alum sample
W = Weight of the sample
A = Number of Hydrogen's

c) Functional groups which impart neither acidic nor basic nature:-

1) Determination of carbonyl compounds:-

Method-I:-

The Carbonyl compounds can be estimated by the gravimetrically as well as volumetrically by heating the compound with Phenyl Hydrazine (or) Di Nitro compound.

Carbonyl compounds are determined by Hydroxyl Amine Hydrochloride.

Principle:-

In excess amount of Hydroxylamine Hydrochloride solution react with carbonyl compound then to form an Oxime ($C_5H_5NO_2$) after then HCL is liberated.

$$\text{Ketone}+NH_2OH.HCL \rightarrow \text{Oxime } (C_5H_5NO_2) + HCL + H_2O$$

However the equilibrium is shifted towards in the presence of Pyridine and then excess amount of $NH_2OH.HCL$ is added. Pyridine is react with HCL, then to form a Pyridine Chloride, which is sufficiently titrated with standard NaOH by using Bromo Phenol blue as an indicator.

$$\text{Ketone}+NH_2OH.HCL+C_5H_5N \rightarrow \text{Oxime } (C_5H_5NO_2) + C_5H_5NHCL + H_2O$$

These liberated HCL can be estimated and the purity of Carbonyl compound can be determined.

Chemicals required:-Sample, $NH_2OH.HCL$, NaOH, Bromo Phenol blue indicator, Standard Methanolic NaOH solution.

Preparation of Hydroxylamine Hydrochloride:-

Dissolve 3.5g of $NH_2OH.HCL$ in about 20mL of distilled water contain in 100mL present measuring flask and make the solution up to the mark with Absolute Ethanol.

Preparation of standard Methanolic NaOH solution:-

Dissolve 2g of NaOH in 12mL of distilled water taken into a 100mL measuring flask and make the solution up to the mark with Methanol. This solution is standardizing the 2N HCL by using Bromo Phenol blue as an indicator.

Preparation of Bromo Phenol blue indicator:-

Mix 5-6 drops of 1% Alcoholic solution of Bromo Phenol blue with 5mL of Pyridine and dilute in to 250mL volume with an absolute Ethyl Alcohol.

Procedure:-

To take 0.02g of sample is taken in to a conical flask. After then to this added 35mL of $NH_2OH.HCL$ solution and then to this added required quantity of Bromo Phenol blue as an indicator. In the solution contains Aldehydes. This solution is stand for 30min and then it is titrated with standard base.

If the sample contains ketone, this solution is stand for water bath at 2hrs. Then this solution is titrated with a standard base.

$$\% \text{ Carbonyl compound} = \frac{(V_1 - V_2) \times N \times M \times 100}{1000 \times W}$$

Here,
V_1 = Volume of NaOH during the blank titration
V_2 = Volume of NaOH during the sample titration
N = Normality of the NaOH
M = Molecular weight of the sample
W = Weight of the sample

Determination of Aldehydes & Ketones:-

Method-I:-

Gravimetric method:-

Principle:-

Ketones:-

When the carbonyl compound react with 2, 4-DNPH compound then to form a Keto 2, 4-DNP, in the presence of ketones.

$$\text{Ketone} + 2,4\text{-DNPH} \rightarrow \text{Keto } 2,4\text{-DNPH}$$

Aldehydes:-

When the carbonyl compound react with 2, 4-DNPH compound then to form an Aldo 2, 4-DNP, in the presence of Aldeydes.

$$\text{Aldehyde} + 2,4\text{-DNPH} \rightarrow \text{Aldo } 2,4\text{-DNPH}$$

Chemicals required: - Sample, 2, 4-DNPH (2, 4 Di Nitro Phenyl Hydrazine), 2N HCL

Preparation of 2, 4-DNPH solution:-

To take 0.4N of 2, 4-DNPH is dissolved in 100mL of 2N HCL at 0^0C. It is separated solution of the reagent.

Procedure:-

To take 0.02g of sample is taken into an Iodine flask. Then to this added 100mL of 2, 4-DNPH solution. Then to a precipitate, then filter the precipitate. Then the residue is taken. Then the residue is washed with 2N.HCL for 2times. Then it is dried at 105^0C-110^0C and weighed.

$$\% \text{ Carbonyl compound} = \frac{W \times F \times 100}{W}$$

Here,

F = Gravimetric factor
W = Weight of the sample
W = Weight of the reagent

Method-II:-

Principle:-

To take the sample is taken into a conical flask. Then to this added Phenyl Hydrazine. After then to this added excess amount of I_2 solution. Then this solution is titrated with hypo by using starch as an indicator.

Chemicals required: - Sample, Phenyl Hydrazine, Hypo ($Na_2S_2O_3$), Iodine, Starch.

Preparation of Hypo ($Na_2S_2O_3$):-

Dissolve 3g of Hypo in 500mL freshly boiled water and cooled and make up to the mark with distilled water.

Preparation of starch:-

0.5g of Starch soluble too little amount of water to make a paste and then to this added 25mL of boiling water with stirring. Boil the content till a clear solution.

Preparation of Iodine:-

Dissolve 3.2g of Iodine and then to this added small quantity of saturated solution of KI. This solution is transfer into a 250mL of measuring flask and make up to the mark with distilled water.

Procedure:-

To take 0.1g of sample is taken into a 500mL round bottom flask. After then to this added 50mL Phenyl Hydrazine reagent then these solutions is reflux for 10min. After then cool the above mixture. Then we are added to the known amount of excess of Iodine and this solution is shaking thoroughly. Then I_2 is liberated, the liberated Iodine is titrated with hypo by using starch as an indicator.

$$\% \text{ Carbonyl compound} = \frac{(V_1-V_2) \times N \times M}{1000 \times W} \times 100$$

Here,

V_1 = Volume of Hypo ($Na_2S_2O_3$) consumed during the blank titration
V_2 = Volume of Hypo ($Na_2S_2O_3$) consumed during the sample titration
N = Normality of Hypo ($Na_2S_2O_3$)
M = Molecular weight of the sample
W = Weight of the sample

2) Determination of Nitro compounds:-

Principle:-

Nitro compounds can be determined by the excess addition of Titanium Chloride (or) Titanium Sulphate to the sample.

Nitro compound converted into amines by the addition of reducing agent. Then untreated Titanium Chloride (or) Titanium Sulphate is titrated with standard Ammonium Ferric Sulphate by using Ammonium Thio Cyanide (NH_4SCN) as an indicator.

Chemicals required: - Sample, $TiCl_3$, $TiSO_4$, Ferric alum, Ammonium Thio Cyanide (NH_4SCN)

Preparation of Titanium Sulphate solution:-

To take 6g of Titanium metal in a flask and then added mixture of 150mL of concentration of H_2SO_4 and 450mL distilled water, warm once water bath and allow of metal is dissolved in takes about 7-8hrs and allow to cool in a stream of CO_2 and dilute to one liter with freshly boiled and cooled distilled water.

Preparation of sample solution:-

Dissolve accurately weighed 0.35g quantity of the compound in a water (or) in a Glacial Acetic acid (or) in an Ethyl Alcohol (it is insoluble in water) and make up to the mark with distilled water.

Preparation of Ammonium Thio Cyanide solution:-

Dissolve 10g of Ammonium Thio Cyanide in distilled water in a 100mL distilled water and make up to the mark.

Procedure:-

To take 25mL of sample solution is taken from the above solution. This is taken into a round bottom flask. After then to this added 25mL of concentration of H_2SO_4. Then this solution is stand for 5min and then passed CO_2 to maintain in inert atmosphere and remove Oxygen in the round bottom flask. After then to this added 50mL of Titanium Sulphate (or) Titanium Chloride. Then this solution is hest for 35-40^{0}C and cooled. Then untreated Titanium Sulphate is titrated with standard Ferric alum by using Ammonium Thio Cyanide as indicator.

$$\% \text{ Nitro compound} = \frac{(V_1 - V_2) \times N \times M \times 100}{1000 \times W \times 6n}$$

Here,
V_1 = Volume of Ferric alum consumed by during blank titration
V_2 = Volume of Ferric alum consumed by during sample titration
N = Normality of Ferric alum
M = Molecular weight of the sample
W = Weight of the sample
6n = Number of Nitro groups

3) Determination of Methoxy group:-

This group is determined by two methods.

i) Gravimetric method:-

Alkoxy Methoxy groups can be estimated by the gravimetrically. Then Methoxy is treated with boiling HI and then produce Alcohol and Methyl Halide is observed in Alcoholic $AgNO_3$.

The Methyl Iodide gives a double salt by the addition of Alcoholic Silver Nitro solution.

$AgNO_3$ is dissolved in the mixture by the addition of concentration of HNO_3 to the mixture AgI remains as precipitate in the flask.

The residue is washed with diluted HNO_3, which is transfer due to crucible and ignited and dried. Remains silver Iodide is weighed.

$$R\text{-}O\text{-}CH_3+HI \rightarrow R\text{-}OH+CH_3I$$

$$CH_3I+AgNO_3 \rightarrow AgIAgNO_3$$

$$AgI\ AgNO_3+HNO_3 \rightarrow AgI$$

$$\%\ \text{Methoxy group} = \frac{\text{Weight of the AgI X Gravimetric factor X 100}}{\text{Weight of the sample}}$$

234.8g AgI = 31.03g $–OCH_3$

ii) Volumetric method:-

Method-I:-

Principle:-

When Methoxy compounds treated with boiling Hydrogen Iodide, then it gives Alcohols and Alkyl Halides. Then Alkyl Halides react with Bromine and it gives Iodic acid. Then produced Iodic acid gives Iodine by the addition of KI in the presence of concentration of H_2SO_4. Then I_2 is liberated. The liberated Iodine is titrated with Hypo by using starch as indicator. The excess amount of Bromine is destroyed as $HBr+CO_2$ the addition of Formic acid.

$$R\text{-}O\text{-}CH_3+HI \rightarrow CH_3I+R\text{-}OH$$

$$CH_3I+Br_2 \rightarrow CH_3Br+IBr$$

$$IBr+2Br_2+H_2O \rightarrow HIO_3+HBr$$

$$HIO_3+5KI \rightarrow I_2$$

$$HCOOH+Br_2 \rightarrow 2HBr+CO_2$$

Chemicals required: - Sample solution, Phenol, Sodium Acetate, Porcelain chips, HI, Bromine, concentration of H_2SO_4, Hypo, Starch, Formic acid, and Troponic acid.

Procedure:-

Accurately weighed about 25g of solid sample is taken into a round bottom flask and then to this added 0.5g of Phenol crystals and 1mL of Propionic Anhydrate also has added a few of Porcelain chips to in now warm the reaction mixture gently dissolve the sample, then attach to the flask to the condenser added 10mL of HI to the neck ‘G’ to the flask. The insert the capillary tube and connect it if the source of CO_2 pass the $CHCl_3$ vapours to the jacket of the lieping condenser ‘B’ for 10min and heat the oil bath gradually the reaction is then complete transfer the content of the receiver ‘D&E’ completely into a 250mL flask contain 10mL of Sodium Acetate solution then added Formic acid with swirling of the flask until the smell of Bromine is not detector. Then the presence of bromine can be tested by adding a block of methyl red indicator. If the colour of indicator is decolourised,it indicates the bromine, then further added few drops of Formic acid dilute the solution to about 100mL added 1g KI and 10mL of 10% H_2SO_4. Stopper the flask and swirling dissolve KI and to mix the contents. Then the liberated Iodine with standard Hypo solution by using starch as indicator.

When a blank titration maybe taken by using phenol and tropoinic anhydrate. It most cases are negligible.

Method-II:-

To take 25g of sample and then to this added 0.5g Phenol crystals and Proponoic Anhydride and few Porcelain chips and 10ml of HI taken into a round bottom flask and it is heated up to 135-150^{0}C and pass to CO_2 gas to maintain the inert atmosphere and remove the O_2 from the round bottom flask and then to this added 10mL of Sodium Acetate & 125mL of distilled water and after few minutes and sufficient amount of Formic acid reacts with Bromine and then to this added 20mL of KI and 10mL of concentration of H_2SO_4. Finally I_2 is liberated, and then liberated I_2 is titrated with Hypo by using starch as an indicator.

Factor:-1mL of Hypo = 0.2586g of Methoxy group (-OCH_3)

4) Determination of Olifinic group:-

Brominating mixture method:-

Principle:-

The olefins are reacted with Bromine, which is produced from the Brominating mixture then to form Bromine substituted Olefins. Then untreated Bromine is reacted Potassium Iodide then Iodine is liberated, the liberated Iodine is titrated with Hypo by using starch as an indicator.

Chemicals required:-Sample, Brominating mixture, KI, Starch, H_2SO_4, Hypo

Preparation of brominating mixture:-

Dissolve 1.5g of Potassium Bromate ($KBrO_3$) and 20g of Potassium Bromite (K Br) in distilled water and make up to the mark with 250mL volumetric flask.

Preparation of Hypo ($Na_2S_2O_3$):-

Dissolve 3g of Hypo in 500mL freshly boiled water and cooled and make up to the mark with distilled water.

Preparation of Potassium Iodide (KI):-

To take 40g of Potassium Iodide is dissolved in 200mL distilled water

Preparation of starch:-

0.5g of Starch soluble too little amount of water to make a paste and then to this added 25mL of boiling water with stirring. Boil the content till a clear solution.

Preparation of sample:-

To take 0.5g of compound, then it is dissolved in a little amount of distilled water. It is insoluble in water. Then it is dissolved in an inorganic solvent like CCl_4 and Chloroform ($CHCl_3$) and make up to the mark in 100mL volumetric flask.

Procedure:-

To take 25ml of sample solution is taken in to a conical flask. Then to this added 5mL of concentration of HCL and then to this added brominating mixture drop wise from burette up to 20mL and then this solution is shake thoroughly for 5min. After then to this added 10mL of concentration of H_2SO_4 and 0.5N of 50mL NaCL solution, this is an act as a catalyst. After then to this added 10mL of KI solution, then Iodine is liberated, the liberated Iodine is titrated with Hypo by using starch as an indicator.

By using Pyridine Sulphate Tri Bromide Mercury Acetate method:-

In this method we have to take 3 measuring flasks.

Flask-I:-

40mL of Glacial Acetic acid and 16.3mL of Pyridine is taken into a flask-I.

Flask-II:-

40mL of Glacial Acetic acid and 10.9mL of concentration of H_2SO_4 are taken into a flask-II. These two mixtures are taken into an about one liter volumetric flask. After then to this added 200mL Acetic acid and H_2SO_4 solution.

Flask-III:-

To take 40mL of Glacial Acetic acid and 5mL of Bromine is taken into a flask-III. Then this solution is shaking thoroughly for 30min and make up to the mark with Glacial Acetic acid.

Procedure:-

To take 0.05g of sample is taken into a round bottom flask. Then to this added 25mL of Glacial Acetic acid and 50mL reagent solution is added to the sample solution. After then to this added 20mL of Mercury Acetate solution. This is an act as catalyst. Then this solution is allow standing for one hour and then to this added sufficient amount of KI and 10mL of water, then Iodine is liberated, the liberated Iodine is titrated with Hypo by using starch as an indicator.

$$\% \text{ olefins} = \frac{(V_1 - V_2) \times 79 \times N}{1000 \times W}$$

Here,

V_1 = Volume of Hypo ($Na_2S_2O_3$) consumed by blank titration
V_2 = Volume of Hypo ($Na_2S_2O_3$) consumed by sample titration
N = Normality of Hypo ($Na_2S_2O_3$)
W = Weight of the sample