# Preface

Analytical chemists and others in many disciplines frequently ask questions such as: What is this substance?; How concentrated is this solution?; What is the structure of this molecule? The answers to these and many other similar questions are provided by the techniques and methods of analytical chemistry. They are common to a wide range of activities, and the demand for analytical data of a chemical nature is steadily growing. Geologists, biologists, environmental and materials scientists, physicists, pharmacists, clinicians and engineers may all find it necessary to use or rely on some of the techniques of analysis described in this book.

If we look back some forty or fifty years, chemical analysis concentrated on perhaps three main areas: qualitative testing, quantitative determinations, particularly by ‘classical’ techniques such as titrimetry and gravimetry, and structural analysis by procedures requiring laborious and time-consuming calculations. The analytical chemist of today has an armoury of instrumental techniques, automated systems and computers which enable analytical measurements to be made more easily, more quickly and more accurately.

I should like to thank all who have contributed to the development of this text, especially our colleagues who allowed us to consult them freely and, not least, the many generations of my students who found questions and problems where we had thought there were none!

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**What is Analytical chemistry?**

Analytical chemistry involves the application of a range of techniques and methodologies to obtain and assess qualitative, quantitative and structural information on the nature of matter.

* **Qualitative analysis** is the identification of elements, species and/or compounds present in a sample.
* **Quantitative analysis** is the determination of the absolute or relative amounts of elements, species or compounds present in a sample.
* **Structural analysis** is the determination of the spatial arrangement of atoms in an element or molecule or the identification of characteristic groups of atoms (functional groups).
* An element, species or compound that is the subject of analysis is known as an

#### analyte.

* The remainder of the material or sample of which the analyte(s) form(s) a part is known as the **matrix**.

#### Purpose:

The gathering and interpretation of qualitative, quantitative and structural information is essential to many aspects of human endeavor, both terrestrial and extra-terrestrial. The maintenance of, and improvement in, the quality of life throughout the world, and the management of resources rely heavily on the information provided by chemical analysis. Manufacturing industries use analytical data to monitor the quality of raw materials, intermediates and finished products. Progress and research in many areas is dependent on establishing the chemical composition of man-made or natural materials, and the monitoring of toxic substances in the environment is of ever increasing importance. Studies of biological and other complex systems are supported by the collection of large amounts of analytical data.

Analytical data are required in a wide range of disciplines and situations that include not just chemistry and most other sciences, from biology to zoology, but the arts, such as painting and sculpture, and archaeology. Space exploration and clinical diagnosis are two quite disparate areas in which analytical data is vital.

Important areas of application include the following.

#### Quality control (QC):

In many manufacturing industries, the chemical composition of raw materials, intermediates and finished products needs to be monitored to ensure satisfactory quality and consistency. Virtually all consumer products from automobiles to clothing, pharmaceuticals and foodstuffs, electrical goods, sports equipment and horticultural products rely, in part, on chemical analysis. The food, pharmaceutical and water industries in particular have stringent requirements backed by legislation for major components and permitted levels of impurities or contaminants. The electronics industry needs analyses at ultra-trace levels (parts per billion) in relation to the manufacture of semi-conductor materials. Automated, computer-controlled procedures for process-stream analysis are employed in some industries.

#### Monitoring and control of pollutants:

The presence of toxic heavy metals (e.g., lead, cadmium and mercury), organic chemicals (e.g., polychlorinated biphenyls and detergents) and vehicle exhaust gases (oxides of carbon, nitrogen and sulfur, and hydrocarbons) in the environment are health hazards that need to be monitored by sensitive and accurate methods of analysis, and remedial action taken. Major sources of pollution are gaseous, solid and liquid wastes that are discharged or dumped from industrial sites, and vehicle exhaust gases.

#### Clinical and biological studies:

The levels of important nutrients, including trace metals (e.g., sodium, potassium, calcium and zinc), naturally produced chemicals, such as cholesterol, sugars and urea, and administered drugs in the body fluids of patients undergoing hospital treatment require monitoring. Speed of analysis is often a crucial factor and automated procedures have been designed for such analyses.

#### Geological assays:

The commercial value of ores and minerals is determined by the levels of particular metals, which must be accurately established. Highly accurate and reliable analytical procedures must be used for this purpose, and referee laboratories are sometimes employed where disputes arise.

#### Fundamental and applied research:

The chemical composition and structure of materials used in or developed during research programs in numerous disciplines can be of significance. Where new drugs or materials with potential commercial value are synthesized, a complete chemical characterization may be required involving considerable analytical work. Combinatorial chemistry is an approach used in pharmaceutical research that generates very large numbers of new compounds requiring confirmation of identity and structure.

# Analysis of Iron ore

#### The main constituents in the analysis of iron ore are

1. **Determination of total iron:**

In aqueous solution, iron may exist as the stable divalent and trivalent states. The determination of total iron consists of reduction of ferric iron into ferrous by SnCl2 and followed by titrating total ferrous iron with a standard potassium dichromate solution.

Iron from the oxide ores can be brought into solution with conc. ***HCl***. 0.5gm of iron ore sample is taken in a conical flask to which 10 ml of conc. ***HCl*** is added. The mixture is first heated gently for 10-15min.The mixture is heated to dryness and then 10ml of conc. ***HCl*** is added. The solution is diluted with distilled water to about 50ml. Heat the contents to boil and add 5% SnCl2 solution (to reduce Fe (III) into Fe (II)) drop wise until yellow colour of Fe (III) disappears. Then cool the solution and add saturated ***HgCl2*** solution until to get a silky white precipitate to oxidize excess SnCl2 if present. Then add 3ml of ortho phosphoric acid, DPA indicator and titrate the total iron against 5/56N ***E2Cr2O7*** solution from the burette until a bluish violet colour appears.

***70oC***

##### SnCl2 + 2FeCl3 SnCl4 + 2FeCl2 2HgCl2 + SnCl2 = Hg2Cl2 + SnCl4

***6Fe2+ + Cr2O72- + 14H+ = Fe3+ + 2Cr3+ + 7H2O***

#### Determination of Ferrous iron:

Ferrous iron present in the iron ore sample can be determined directly by dissolving 0.5g of the ore sample in 10ml conc.HCl , add 3ml of ortho phosphoric acid and DPA indicator and titrate the Ferrous iron against 5/56N ***E2Cr2O7*** solution from the burette until a bluish violet colour appears.

#### Determination of Silica

Mix 0.5g of iron ore sample with 3-4g of fusion mixture and heat mixture in Pt crucible at 950oC. Cool the crucible and extract the molten liquid into minimum amount of 1:1 ***HCl***. Boil and evaporate to dryness on a hotplate. Cool and dissolve the residue in 30ml of Conc.***HCl*** solution and dilute to known volume. Boil the contents and filter through paper pulp. Ignite the residue and weigh. From the weight of residue amount of silica can be calculated.

To obtain more accurate result the residue obtained above is moistened with few drops of ***H2SO4*** and add 1-2ml of ***HF***. Evaporate to dryness and ignite again. Silica volatilizes as ***SiF4***. Weight the residue again and the difference between weights will give the amount of Silica.

#### The filtrate obtained after the removal of Silica is used to determine Al2O3, CaO, MgO and TiO2.

The filtrate is oxidized with 1-2ml of Conc. HNO3 and boiled to reduce the volume to about 100ml. cool the solution and add 2ml of Bromine solution, add 5-10g of NH4Cl and excess of NH3. Filter through filter paper and collect the filtrate. Wash the precipitate with hot water and dissolve it in Conc. HCl. Reserve the filtrate for the determination of CaO and MgO. The precipitate is used for the determination of Al2O3 and TiO2

#### Determination of Alumina:

Dissolve the precipitate obtained in Conc. ***HCl*** and add 15ml of Saturated Solution of Sodium Phosphate and ***NH4OH*** Solution till white precipitate is formed. This precipitate is dissolved in ***HCl***. To the resulting solution 15ml of acetic acid and 10- 15gm of ***sodium thiosulphate*** crystals are added to keep the iron in solution in Ferrous state. The solution is then boiled for 5minutes and ammonium acetate solution is added. Then aluminum precipitates as ***AlPO4***. Filter the precipitate and ignited at 900oC for 5minutes, cooled and weighed as ***Al2O3***

Percentage of ***Al2O3*** = weight of residue x 0.4178/weight of sample x 100

#### Determination of Lime (CaO):

The filtrate obtained after Bromine and ***NH4OH*** treatment and separation of iron and aluminium precipitates, it is boiled and then add 5gms of ammonium oxalate is added. The solution is digested for 30 minutes and maintaining the solution alkaline with ***NH4OH***. The precipitate of calcium oxalate formed. Filter off the precipitate and reserve the filtrate for the determination of ***MgO***.

The precipitate is transferred into a beaker and dissolved in dil. ***H2SO4*** solution. Heat the solution gently and titrate the liberated oxalate with a standard ***EMnO4*** solution until permanent pink colour appears. The amount of ***CaO*** can be calculated as,

1ml of 0.1N ***EMnO4*** == 0.0028 gm of ***CaO***

#### Determination of MgO:

Estimation of ***MgO*** is based on precipitation Mg as magnesium ammonium phosphate and decomposing as magnesium pyro phosphate.

The filtrate obtained after the removal of calcium, is neutralized with ***HCl*** and made the solution slightly acidic. The solution is diluted to known volume. Then for each 100ml add 20ml of 10% diammonium phosphate ***[(NH4)2HPO4]*** solution is added. The solution is stirred vigorously and add ***NH4OH*** drop wise until the solution is slightly basic. Then magnesium is precipitate as magnesium ammonium phosphate. The precipitate is allowed to settle for about 5 hours and filtered through filter paper. The precipitate is taken in a porcelain crucible and ignited at about 900oC until a constant weight is obtained. The precipitate decomposes into magnesium pyrophosphate (***Mg2P2O7***). The residue is weighed as ***Mg2P2O7*** from which MgO can

be calculated.

***MgO*** = 0.3622 x weight of ***Mg2P2O7***x100

#### Determination of sulphur:

Sulphur exists in iron ore as MnS. To determine the sulphur, weigh 1g of ore sample and transfer into beaker. Add a mixture of 40ml of ***HNO3*** and 5ml of ***HCl*** and heat in a fume chamber for 5ml liquid remains in the beaker. Add a pinch of pure ***Na2CO3*** (to fix the Sulphate formed by aqua regia in the form of ***Na2SO4***) and evaporate to dryness. Cool the residue and dissolve in 25ml of Conc.***HCl*** and dilute to 50ml. Then remove all the ***iron*** by adding an excess of ammonia solution as ***Fe(OH)3***.

Neutralize the filtrate with ***HCl*** , boil the solution and add 100 ml of ***BaCl2*** solution. Stir vigorously and allowed to stand for 30min. filter the precipitate and dry until constant weight is obtained. The precipitate is weighed as ***BaSO4***.

Percentage of sulphur = weight of ***BaSO4***x 0.1374x100

#### Determination of total manganese:

The filtrate obtained after the removal of magnesium is taken and 50ml of ***HNO3*** and 1gm of ***NaBiO3*** is added to the solution. The solution is then heated to boiling and ***H2SO3*** is added to reduce any excess of ***NaBiO3***. The solution is boiled for 5min to expel nitrogen and cooled to 15oC. Then 4-5gm of ***NaBiO3*** is added and the solution is filtered.

To the filtrate a measured quantity of excess of standard ferrous ammonium sulphate is added and back titrate the excess un reacted ferrous ammonium sulphate with standard ***EMnO4*** solution. From the volume of mohr’s salt solution required to react with permanganic acid the amount of Mn can be calculated as,

1ml of 0.1N Mohr’s salt solution = 0.0010988gm of Mn.

#### Determination of *P2O5*:

Phosphorous in ores can be brought up into solution with aqua regia in the form of ortho phosphate which can be precipitated as **ammonium phosphomolybdate** by the addition of ammonium molybdate in the presence of nitric acid.

Dissolve 2g of ore sample in 40ml of conc. ***HCl*** in a beaker and evaporate to dryness. Redissolve in 20 ml of ***HCl*** and dilute to with 30 ml water. Filter the residue and reserve the filtrate. Ignite the residue in a platinum crucible and fuse with 2-3g of ***Na2CO3***. Extract the fused mass with hot water. Combine this solution with filtrate. Add 30ml of conc. ***HNO3*** heat the solution to boiling and add ***EMnO4*** solution drop wise until pink colour observed (to convert meta phosphoric acid into ortho). Continue boiling and destroy the excess ***EMnO4*** with ***Na2SO3***. Now add 40ml of Ammonium Molybdate solution, shake and filter.

Transfer the precipitate into a beaker and add a known volume of excess standard ***NaOH*** solution. Then titrate the excess unreacted ***NaOH*** solution with a standard ***HNO3*** solution. From the consumed volume the amount of Phosphorous can be calculated,

##### P + 11HNO3 = PH3 3PH3 + 8HNO3 = 3H3PO3

***3H3PO3 + EMnO4 = 3H3PO4***

***H3PO4 + 21HNO3 + 12(NH4)2MoO4 = (NH4)3PO4.12MoO3 + 21NH4NO3 2[(NH4)3PO4.12MoO3] + 46NaOH = 2(NH4)2HPO4 + (NH4)2MoO4 + 28Na2MoO4 +***

***22H2O***

1. **Determination of Titania**

If appreciable amount of ***TiO2*** is present in the ore, it will be precipitated along with ***AlPO4***. To determine the percentage of ***TiO2***, fuse the ignited ***AlPO4*** with 2-3gms of fusion mixture in a crucible. Extract the melt with hot water. The ***Al2O3*** remains in the solution while ***TiO2*** is precipitated. Filter off the precipitate and add 1g of potassium bisulphate. Carefully fuse the mixture for 5min and melt the extract with 30 ml of 5% ***H2SO4***. Dilute to known volume and add 2ml of ***H2O2*** and compare the yellow colour developed with a standard solution of ***TiO2***.

2gm of ore is decomposed by fusion with potassium pyrosulphate in a platinum crucible the fused mass is dissolved water, ***HCl*** and ***H2SO4***. The solution is reduced with zones redactor. Then the reduced solution is titrated with a standard solution of ferric ammonium sulphate using ammonium thiocyanate solution as indicator. From the volume of ferric ammonium sulphate the percentage of ***TiO2*** can be calculated

%***TiO2*** = 0.007991 x volume of 0.1N Ferric alum /weight of sample x100

#### Determination of Alkali

5g of ore is dissolved in HCl and few drops of ***HNO3*** and evaporate to dryness. The dried mass is redissolved in 15ml of ***HCl*** and 30ml of water. The insoluble residue is ignited in a platinum crucible and treated with ***H2SO4*** and sufficient HF to decompose silicates and dissolve the residue in water. The solution is added to previous filtrate. Then add ***BaCl2*** solution and filter off ***BaSO4***. ***BaCl2*** transforms alkali sulphates into chlorides. The filtrate is heated and added an excess of ammonium carbonate solution. The filtrate is evaporated to dryness and weighed as mixture of ***ECl*** and ***NaCl***.

To the residue a little water is added to dissolve and then platinic chloride and equal amount of alcohol are added. Then a residue of potassium platinic chloride ***(E2[PtCl6]*** will separate out. Filter off the crystals, dry at 120oC and weigh. From the weight ***ECl*** can be calculated as,

***ECl*** = 3/5 x 0.3071xweight of ***(E2[PtCl6] NaCl*** = weight of (***NaCl+ECl***)-weight of ***ECl***

#### Loss on ignition

1gm of sample is taken in a platinum crucible and ignited at 950-1000oC for 30minutes. The ignited sample is cooled in a desiccator and weighed. The loss in weight will represent the loss on ignition

#### Estimation of combined water

1gm of sample is taken in a porcelain boat and inserted in a glass tube having stoppers at both ends. A suitable dessicant such as ***CaCl2*** is connected at the inlet of the tube and exit end is connected to a pre weighed calcium chloride tube. Then the boat is heated upto 300oC. After heating ***CaCl2***tube is reweighed.

#### % of Combined water = increase in weight/weight of sample x 100



**2. Analysis of manganese ore**

Manganese ore is the principal raw material for the manufacture of ferro manganese and electrolytic manganese

#### Determination of silica and barium oxide

Digest one gram of ore with 20ml of HCl and evaporate to dryness. Redissolve the residue in HCl. Add 10ml of dil H2SO4 and evaporate to fumes. Add 150ml of water and boil, allow stand and filter. Collect the filtrate in a 500ml flask. Ignite the residue in a platinum crucible and weigh. This weight represents the weight of SiO2 and BaSO4.

Treat the ignited residue in a crucible with conc. H2SO4 and HF to expel SiO2 as SiF4. Ignite and weigh the residue. The loss of weight represents the SiO2.

Fuse the residue left after the removal of SiO2 with about 1g of Na2CO3. Extract melt with dil.HCl. add a little dil.H2SO4 and adjust the acidity of the solution with NH4OH. Allow to stand , filter , ignite and weight as BaSO4. Add the filtrate to the main filtrate in 500ml flask.

#### Determination of iron and aluminium oxides:

Take 100ml of the solution from the measuring flask and add NH4Cl and excess of NH4OH. Filter off iron aluminium as hydroxides. Dissolve the precipitate in HCl and Al can be estimated by “phosphate method”. Boil the filtrate with 1ml of Conc. HNO3 and precipitate iron with NH4Cl and excess of NH4OH. Redissolve the precipitate in HCl and estimate iron by K2Cr2O7 method.

#### Determination of total manganese by Volhard method:

Take 100ml of the solution from the above prepared and heat to boiling. Precipitate Fe as Fe(OH)3 by adding zinc oxide emulsion. This is indicated by the milkiness of the upper layer of the solution. NH4OH or NaOH is not used as a precipitant, as they will precipitate both Fe and Mn. To the filtrate add few drops of

dil.HNO3 and titrate with standard KMnO4 solution. The end point is indicated by the appearance of pink colour.

3MnSO4 + 2KMnO4 + 7H2O = 5MnO2.H2O + K2SO4 + 2H2SO4

1ml N/10 KMNO4 = 0.001648g of Mn

#### Determination of MnO2:

Take 0.5g of finely ground ore and add about 40ml of a 20% solution of H2SO4. Then add a known volume of oxalic acid solution warm until it dissolves. Dilute to 250ml and take a known volume of it and add 5 ml dil H2SO4 and warm to 60oC and titrate with standard KMnO4 solution.

MnO2 + H2C2O4 + H2SO4 = MnSO4 + 2CO2 + 2H2O

5H2C2O4 + 2KMnO4 + 3H2SO4 = 2MnSO4+ K2SO4 + 10CO2 + 8H2O

#### Determination of Lime:

The filtrate obtained after removal of Fe and Al add bromine and ammonia to precipitate Mn as MnO2. Filter off MnO2. To the filtrate NH4OH and ammonium oxalate solution to precipitate calcium oxalate. Filter off the precipitate and dissolve in H2SO4 and titrate with 0.1N KMNO4 solution.

#### Determination of total Sulphur:

Take 2.0g of finely ground ore and dissolve in a aqua regia and filter. Fuse the residue with Na2CO3 in a platinum crucible which produces Na2SO4 and BaCO3. Separate Na2SO4 by dissolving in water and filtering. Acidify the filtrate with HCl. Evaporate to dryness. Cool. Redissollve in dil.HCl and dilute with water. Filter off any residue of SiO2. Mix the two filtrates. Adjust the acidity with NH4OH and add BaCl2 filter, ignite and weigh the residue as BaSO4.

#### Determination of Phosphorous:

Take 2.0g of the ore with HCl filter off the insoluble residue and treat with Conc.H2SO4 and HF. Add the resulting Sulphate solution to the filtrate. Add ammonia

until a precipitate forms. Redissolve in HNO3, heat to 75oC add ammonium molybdate to precipitate Phosphorous as ammoniumphosphomolybdate. Dissolve the precipitate in a measured excess of a standard NaOH solution and finish by the alkalimetric titration as given in iron ore.



# 3. Analysis of Chromite ore

Chromite(FeO.Cr2O3) is the main source of chromium metal. It is also used in the manufacture of ferro-chrome and chrome bricks.

#### Determination of chromic oxide:

Take .05g of finely ground ore and mix it with about 3-4 g of sodium peroxide in a nickel crucible. Fuse the contents by slow heating for 10-15minutes and cool. Add 2g more of sodium peroxide and fuse again about 10minutes. Extract the fused mass into a beaker containing 300ml of water. Boil for 10 minutes to decompose H2O2 formed by Na2O2. Filter and cool.

To the cooled filtrate add conc. H2SO4 to make the solution acidic. Boil the solution and add 5% solution of KMnO4 until pink colour persists. This is added to destroy H2O2. Continue to boiling and add 10-15ml of HCl, 200ml of water. Continue to boiling until smell of chlorine is given off. If H2O2 is present it will reduce chromate, hence KMnO4 is added to destroy H2O2 and the excess KMnO4 is destroyed by adding HCl.

To the cooled solution add an excess of standard solution of Ferrous ammonium sulphate and titrate back the excess of ferrous ammonium sulphate added by a standard solution of KMnO4 or K2Cr2O7 solution using DPA as an indicator by usual procedure until bluish violet colour appears.

Na2Cr2O7 + 6FeSO4 +7H2SO4 = Cr2(SO4)3 + 3Fe2(SO4)3 + Na2SO4 + 7H2O

335 parts of Fe = 152 parts of Cr2O3 or 104 parts of Cr.

#### Determination of Silica

Weigh 1g of the ore sample and fuse with Na2O2 exactly as done in above case. The silica of the ore will be converted into sodium silicate. Extract the fused mass with water and add excess of dil.HCl and evaporate to dryness and redissolve in dil.HCl and filter. Dry the residue and weigh as SiO2. The residue may be treated further with dil.H2SO4 and HF which gives the more precise result of SiO2.

#### Determination of ferrous oxide:

To the filtrate obtained after the removal of Silica add 3g of NH4Cl and then add an excess of ammonia. Boil and filter the precipitate of iron, aluminium and chromium hydroxides. Dissolve the precipitate in dil HCl. Boil the solution and add SnCl2 solution to reduce Fe(III) in Fe(II) and remove the excess SnCl2 by adding HgCl2 if present. Now titrate the Fe(II) present in the solution with a standard solution of 5/56N K2Cr2O7 using DPA indicator until bluish violet colour appears.

#### Determination of Alumina:

Weigh 1g of the ore sample and fuse with Na2O2 exactly as described under above case. Extract the melt with water and boil the solution and filter. Acidify the filtrate with dil.HCl and add an excess of ammonium phosphate solution. Al precipitates as AlPO4. Filter the precipitate and ignite at 900OC for 10-15minutes and weigh.

#### Determination of Lime (CaO):

Take the residue in the determination of Al which contains iron, calcium and magnesium oxides. Dissolve the residue in dil.HCl and make the solution alkaline by adding ammonia. Filter off the precipitate and boil the filtrate, add ammonium solution and ammonium oxalate solution to precipitate Calcium as calcium oxalate. Filter off the precipitate and dissolve it in Dil.H2SO4 and boil. Titrate the liberated oxalate ions with a standard NaOH solution and report the amount of lime from the titrated data.

#### Determination of magnesia (MgO):

Boil the filtrate obtained after the precipitation of calcium as oxalate and add few drops of ammonia. Then add an excess of ammonium phosphate solution. Filter the magnesium ammonium phosphate precipitate and ignite at 1000OC until constant weight is obtained. From the residue the amount of magnesia can be calculated.

# 4. Analysis of Bauxite

**Bauxite** is a sedimentary rock with a relatively high aluminium content. It is the world's main source of aluminium. Bauxite consists mostly of the aluminium minerals. The ore must first be chemically processed to produce alumina (aluminum oxide). Alumina is then smelted using an electrolysis process to produce pure aluminum metal. It was first discovered in France (1821) in the vicinity of a place called Les Baux, after which it was named.

#### Determination of silica

Mix 1g of iron ore sample with 3-4g of fusion mixture and heat mixture in Pt crucible at 950oC. Cool the crucible and extract the molten liquid into minimum amount of 1:1 ***HCl***. Boil and evaporate to dryness on a hotplate. Cool and dissolve the residue in 30ml of Conc.***HCl*** solution and dilute to known volume. Boil the contents and filter through paper pulp. Ignite the residue and weigh. From the weight of residue amount of silica can be calculated.

To obtain more accurate result the residue obtained above is moistened with few drops of ***H2SO4*** and add 1-2ml of ***HF***. Evaporate to dryness and ignite again. Silica volatilizes as ***SiF4***. Weight the residue again and the difference between weights will give the amount of Silica.

#### Determination of Ferric oxide

100ml of sample solution obtained after the removal of Silica is taken for iron estimation. Heat the contents to boil and add 5% SnCl2 solution (to reduce Fe (III) into Fe (II)) drop wise until yellow colour of Fe (III) disappears. Then cool the solution and add saturated ***HgCl2*** solution until to get a silky white precipitate to oxidize excess SnCl2 if present. Then add 3ml of ortho phosphoric acid, DPA indicator and titrate the total iron against 5/56N ***E2Cr2O7*** solution from the burette until a bluish violet colour appears.

***70oC***

##### SnCl2 + 2FeCl3 SnCl4 + 2FeCl2 2HgCl2 + SnCl2 = Hg2Cl2 + SnCl4

***6Fe2+ + Cr2O72- + 14H+ = Fe3+ + 2Cr3+ + 7H2O***

#### Determination of TiO2:

1gm of ore is decomposed by fusion with potassium pyrosulphate in a platinum crucible the fused mass is dissolved water, ***HCl*** and ***H2SO4***. The solution is reduced with zones redactor. Then the reduced solution is titrated with a standard solution of ferric ammonium sulphate using ammonium thiocyanate solution as indicator. From the volume of ferric ammonium sulphate the percentage of ***TiO2*** can be calculated

%***TiO2*** = 0.007991 x volume of 0.1N Ferric alum /weight of sample x100

#### Determination of Alumina:

100ml of sample solution obtained after the removal of Silica is taken and nuetralised with NH4OH and few drops of NH4OH is added inexcess and boiled for few minutes. Dissolve the precipitate obtained in Conc. ***HCl*** and add 15ml of Saturated Solution of Sodium Phosphate and ***NH4OH*** Solution till white precipitate is formed. This precipitate is dissolved in ***HCl***. To the resulting solution 15ml of acetic acid and 10- 15gm of ***sodium thiosulphate*** crystals are added to keep the iron in solution in Ferrous state. The solution is then boiled for 5minutes and ammonium acetate solution is added. Then aluminum precipitates as ***AlPO4***. Filter the precipitate and ignited at 900oC for 5minutes, cooled and weighed as ***Al2O3***

Percentage of ***Al2O3*** = weight of residue x 0.4178/weight of sample x 100

Alternatively wash and ignite the precipitate obtained after adding NH4OH and this precipitate represents Fe2O3,TiO2 and Al2O3. Deduct the weights of Fe2O3 and TiO2 te get the amount of Al2O3.

#### Determination of manganese oxide:

The filtrate obtained after the removal of Iron, Aluminium, Titanium etc is taken in a 500ml beaker and add Bromine water and small excess of NH4OH is are added. The solution is boiled and filtered quickly. The precipitate is ignited at high temperature, cooled and weighed as Mn3O4. The percentage of MnO can be calculated as,

%Mn = weight of residue/Wt. of sample x 0.93 x 100% Mn can also be determinaed by Volhard method .

#### Determination of P2O5:

Phosphorous in ores can be brought up into solution with aqua regia in the form of ortho phosphate which can be precipitated as **ammonium phosphomolybdate** by the addition of ammonium molybdate in the presence of nitric acid.

Dissolve 2g of ore sample in 40ml of conc. ***HCl*** in a beaker and evaporate to dryness. Redissolve in 20 ml of ***HCl*** and dilute to with 30 ml water. Filter the residue and reserve the filtrate. Ignite the residue in a platinum crucible and fuse with 2-3g of ***Na2CO3***. Extract the fused mass with hot water. Combine this solution with filtrate. Add 30ml of conc. ***HNO3*** heat the solution to boiling and add ***EMnO4*** solution drop wise until pink colour observed (to convert meta phosphoric acid into ortho). Continue boiling and destroy the excess ***EMnO4*** with ***Na2SO3***. Now add 40ml of Ammonium Molybdate solution, shake and filter.

Transfer the precipitate into a beaker and add a known volume of excess standard ***NaOH*** solution. Then titrate the excess unreacted ***NaOH*** solution with a standard ***HNO3*** solution. From the consumed volume the amount of Phosphorous can be calculated, ***P + 11HNO3 = PH3***

##### 3PH3 + 8HNO3 = 3H3PO3

***3H3PO3 + EMnO4 = 3H3PO4***

***H3PO4 + 21HNO3 + 12(NH4)2MoO4 = (NH4)3PO4.12MoO3 + 21NH4NO3***

***2[(NH4)3PO4.12MoO3] + 46NaOH = 2(NH4)2HPO4 + (NH4)2MoO4 + 28Na2MoO4 +***

***22H2O***

1. **Determination of Lime (CaO):**

The filtrate obtained after the removal of Mn can be used for the determination of lime. The filtrate is evoperate to dryness and ammonium salts are decomposed by heating.the residue is dissolved in 10ml of HCl. It is boiled and then add 5gms of ammonium oxalate is added. The solution is digested for 30 minutes and maintaining the solution alkaline with ***NH4OH***. The precipitate of calcium oxalate formed. Filter off the precipitate and reserve the filtrate for the determination of ***MgO***.

The precipitate is transferred into a beaker and dissolved in dil. ***H2SO4*** solution. Heat the solution gently and titrate the liberated oxalate with a standard ***EMnO4*** solution until permanent pink colour appears. The amount of ***CaO*** can be calculated as,

1ml of 0.1N ***EMnO4*** == 0.0028 gm of ***CaO***

#### Determination of magnesia (MgO):

Estimation of ***MgO*** is based on precipitation Mg as magnesium ammonium phosphate and decomposing as magnesium pyro phosphate.

The filtrate obtained after the removal of calcium, is neutralized with ***HCl*** and made the solution slightly acidic. The solution is diluted to known volume. Then for each 100ml add 20ml of 10% diammonium phosphate ***[(NH4)2HPO4]*** solution is added. The solution is stirred vigorously and add ***NH4OH*** drop wise until the solution is slightly basic. Then magnesium is precipitate as magnesium ammonium phosphate. The precipitate is allowed to settle for about 5 hours and filtered through filter paper. The precipitate is taken in a porcelain crucible and ignited at about 900oC until a

constant weight is obtained. The precipitate decomposes into magnesium pyrophosphate (***Mg2P2O7***). The residue is weighed as ***Mg2P2O7*** from which MgO can be calculated.

***MgO*** = 0.3622 x weight of ***Mg2P2O7***x100

#### Determination of alkali:

5g of ore is dissolved in HCl and few drops of ***HNO3*** and evaporate to dryness. The dried mass is redissolved in 15ml of ***HCl*** and 30ml of water. The insoluble residue is ignited in a platinum crucible and treated with ***H2SO4*** and sufficient HF to decompose silicates and dissolve the residue in water. The solution is added to previous filtrate. Then add ***BaCl2*** solution and filter off ***BaSO4***. ***BaCl2*** transforms alkali sulphates into chlorides. The filtrate is heated and added an excess of ammonium carbonate solution. The filtrate is evaporated to dryness and weighed as mixture of ***ECl*** and ***NaCl***.

To the residue a little water is added to dissolve and then platinic chloride and equal amount of alcohol are added. Then a residue of potassium platinic chloride ***(E2[PtCl6]*** will separate out. Filter off the crystals, dry at 120oC and weigh. From the weight ***ECl*** can be calculated as,

***ECl*** = 3/5 x 0.3071xweight of ***(E2[PtCl6] NaCl*** = weight of (***NaCl+ECl***)-weight of ***ECl***

#### Determination of Vanadium:

3-4gm of sample is taken into a 500ml beaker to which 100ml of acid mixture is(350ml water,250ml1:1 H2SO4,200ml HNO3 and 200ml HCl) is added. The beaker is covered and heated to heavy fumes of SO2. The resulting mass is cooled and diluted to about 100ml and boiled to dissolve salts. The solution is filtered on a medium paper and the residue is washed with hot water. 30ml of HCl is added to the filtrate and then diluted to 300ml and cooled to about 100C. Ice cold Cupferron solution is added and stirred until precipitation is complete. The precipitate is allowed to stand for 10minutes. The precipitate is filtered off and dried at 6000C in a Platinum crucible. The residue is fused with sodium carbonate and extracted into hot water. 10ml of 1:1 H2SO4 is added to the extracted solution and heated to boiling with an addition of excess of KMnO4 dropwise until a strong pink colour is developed. The solution is cooled and added an excess of 0.1N ferrous ammonium sulphate is added. Then the

solution is titrated with standard KMnO4 solution until the colour changes to pale pink.

5VO2+ + MnO4- + 6H2O = 5 VO3-+ Mn2+ + 12H+ VO3- + Fe2+ + 4H+ = VO2+ + Fe3+ + 2H2O

#### Vanadium = 0.005095 x ml of 0.1N KMnO4

1. **Determination of Zirconium:**

3-4gm of finely ground ore sample is taken into a platinum crucible to which 10ml of HNO3, 20ml of HF and 20ml of H2SO4 are added.the mixture is evoperated to fumes, cooled and 50ml of water and 20ml of HCl are added. The mixture is then heated to dissolve the salts. If any insoluble residue remains, it is fused with fusion mixture and extracted into H2SO4. The resulting solution is added to filtrate. The solution is adjusted to 200ml, cooled to 100C and ice cold cupferron solution is added until precipitate turns reddish brown indicating partial precipitation of iron. The solution is allowed to stand for 15minutes and filtered off. Ignite the residue at 6000C. The residue is then fused with KHSO4 and extract the fused mass into dil H2SO4 . To the solution 5ml of H2O2 and 10ml of Ammonium Phosphate are added and allowed to stand for 12 hours at 60-700C. the precipitate formed is filtered off and ignited at 11000C. the ignited residue is colled and weighed as Zr2P2O7.

#### Percentage of ZrO2= 0.4647 x weight of ppt.

**5. Analysis of Soaps**

A soap is a salt of a compound known as a fatty acid. A soap molecule consists of a long hydrocarbon chain with a carboxylic acid group on one end which is ionic bonded to a metal ion, usually a sodium or potassium. The hydrocarbon end is nonpolar and is soluble in nonpolar substances (such as fats and oils), and the ionic end (the salt of a carboxylic acid) is soluble in water.

#### Determination of Moisture & Volatile Matter

Accurately weigh 5 *g of the soap sample in a dish*, and dry in a hot air oven to constant mass at a temperature of 105 ± 2°C. Cool in a desiccator and weigh. The difference in weight will give the moisture content of soap.

#### Determination of Total Alkali.

Ignite the residue from the moisture determination at a low red heat until all carbonaceous matter is burned off. Weigh the mineral residue, which consists of Na2CO3 or K2CO3 (also SiO2, NaCl, etc., if present). Pour boiling water into the dish and warm until the residue is dissolved. Cool, and titrate with 0.1 N acid and methyl orange. If the residue is not completely soluble in water, the insoluble matter should be filtered off and the filtrate evaporated to dryness, ignited and weighed before titration.

#### Determination of Total Fatty Matter.

Pipette 200 cc. of the original hot soap solution into a beaker, add dil. HNO3 until slightly acid, heat on the water bath until the fatty acids have collected in a clear layer on top and the solution below is perfectly clear. Cool in ice water or let stand overnight. Remove the layer of fatty acids to a beaker. Shake out the clear liquid in a separatory funnel with 2 portions of 50 cc. each of CHCl3 to remove the rest of the fatty matter. Transfer the CHCl3 extract to the beaker containing the fatty cake and dissolve the latter. Transfer the CHCl3 solution to a separatory funnel, rinsing the beaker with CHCl3. Wash the CHCl3 extract -with 2 portions of 20 cc. of water.

Evaporate off the CHCl3, dry at 1000 C. to constant weight and weigh as total fatty matter.

#### Determination of Free Caustic Alkali or Free Fatty Acids.

Dissolve 5 grams of soap in warm neutral 95% alcohol. Filter, using a hot water funnel; wash with hot alcohol; titrate the filtrate with 0.1 N acid and phenolphthalein and calculate to NaOH or KOH; as the case may be. If the filtrate is acid, titrate with

0.1 N caustic and calculate to oleic acid.

**CALCFLATION.** 1ml 0.1 N acid =0.00400 gram NaOH.

I ml 0.1 N acid =0.00561 gram KOH. 1ml 0.1 N alkali = 0.0282 gram oleic acid.

#### Determination of Sodium Silicate.

The presence of sodium silicate is generally indicated by the fact that the weight of ash is greater than the weight calculated from titration, provided of course that insoluble abrasives are not present. The amount of sodium silicate may be ascertained by determining SiO2 in the soluble ash after titration for total alkali. Add a slight excess of HC1, evaporale to dryness, and finally bake for one hour at 1300C. Take up with conc. HC1, dilute with hot water, filter, wash, ignite very strongly and weigh as

SiO2 . From this weight calculate to Na2Si4O9.

#### CALCFLATION. SiO2 X 1.257 = Na2Si4O9

1. **Determination of Chlorides**.

Evaporate the filtrate from the fatty acids to about 100 ml. Neutralize carefully with CaCO3, and titrate with 0.1N AgNO3, using K2CrO4 as indicator.

For the determination, pipette 50 ml of the HNO3 solution into a clean porcelain dish or casserole. Add sufficient pure CaCO3 to neutralize all the acid present and still have an excess of the CaCO3 undissolved. Then add about 5 ml of K2CrO4 indicator solution and titrate the Cl- with 0.1 N AgNO3 until a permanent reddish color appears in the solution. The end point can best be determined in the presence of artificial light. Calculate the amount of chlorine to which the titration corresponds. Divide this weight by 0.05 of the weight of the original sample and multiply by 100 to obtain the percentage of Cl.

#### 1 ml of 0.1 N AgNO3 = 0.00585 gram NaCl. = 0.00746 gram *ECl*

**6. Analysis of Oils and Fats**

Fats and oils are recognized as essential nutrients in both human and animal diets. They provide essential fatty acids which are the building blocks for the hormones needed to regulate bodily systems. Carrier for the oil soluble vitamins A, D, E, and

K. They also enhance the foods we eat by providing texture and mouth feel, imparting flavor, and contributing to the feeling of satiety after eating. Oils and fats are a rich source of dietary energy and contain more than twice the caloric value of equivalent amount of sugar.

Fats and oils are constructed of building blocks called “**triglycerides**” resulting from the combination of one unit of **glycerol** and three units of **fatty acids**. They are insoluble in water but soluble in most organic solvents. They have lower densities than water, and may have consistencies at ambient temperature of solid, semisolid, or clear liquid. When they are **solid-appearing** at a normal room temperature, they are referred to as “**fats**,” and when they are **liquid** at that temperature, they are called “**oils**.”

“Essential” fatty acids have been generally regarded as those which are required by humans but are not synthesized by the body and must be obtained through the diet. Linoleic and linolenic acids are essential fatty acids. They serve as substrates for the production of polyunsaturated fatty acids.

#### 1. Acid value (Acid Number):

The acid value (*AV) is* the number of milligrams of potassium hydroxide required to neutralize the free acids present in 1 g of an oil sample.

* Acid value is the measure of hydrolytic rancidity. In general, it gives an indication about edibility of the oil.
* Edible oil contain > 1%

#### Required solutions:

1. Fat or Oil 2. Absolute ethanol alcohol

1. Phenolphthalein 4) 0.1 N KOH

#### Procedure :

Place 5.0 g of fat or oil in a dried conical flask. Add 25 ml of absolute ethanol alcohol and add ( 2-3) drops of phenolphthalein Heat with shaking in water bath for 10 minutes ,then cool and titrate the solution against 0.1 N KOH until pink color appears (end point)

Calculate the acid value (AV) and free fatty acid (%FFA). Acid Value (AV) = mL of KOH x N x 56 / weight of sample

%Free Fatty Acid (FFA) = Acid Value x 0.503 N = Normality of KOH

#### Saponification Value :

The saponification value is the number of mg of potassium hydroxide required to neutralize the free acids and to saponify the esters in 1 g of the substance. The saponification number is a measure of the average molecular weight of the triacylglycerols in a sample. Saponification is the process of breaking down a neutral fat into glycerol and fatty acids by treatment with alkali.

Saponification value is a valuable characteristic of oils and fats, which indicates the chain length of the fatty acids present The common vegetable oils exhibit SVs ranging from 160 to 264. SV of mustard oil of about 170-180 is due to the presence of glycerides. 250-264 for coconut oil is indicative of shorter chain acids.

Required Solutions:

1. Fat or Oil
2. 0.5 N alcoholic potassium hydroxide ( alcoholic KOH) prepared by dissolving 30 g potassium hydroxide in 20 mL of water and make the final volume to 1 L using 95 % ethanol. Leave the solution to stand for 24 h before decanting and filtering the solution.
3. 0.5 N Hydrochloric acid
4. Phenolphthalein.

#### Procedure :

Weigh approximately 2 g of the fat or oil into a 250 mL conical flask. Add 25 mL of alcoholic potassium hydroxide solution ( 0.5 N). Attach a reflux condenser and heat the flask contents on a boiling water bath for 1 hour with occasional shaking. While the solution is still hot , add 3 drops of phenolphthalein indicator and titrate the excess potassium hydroxide with the 0.5 N hydrochloric acid ( Vml of hydrochloric acid at end point represents S). Do same above procedure but without sample ( Vml of hydrochloric acid at end point represents B). calculate the saponification number.

Saponification value = 56.1 x (B – S) N / W

Where, B = volume in ml of standard Hydrochloric acid solution required for the blank.

S = volume in ml of standard Hydrochloric acid solution required for the sample. N = normality of the standard sodium Hydrochloric acid solution.

W = weight in g of the sample.

#### Typical Saponification Value of Fats and Oils

Butter fat and vegetable fats

|  |  |
| --- | --- |
| Fat or oil | Saponification Value |
| Milk fat | 210-233 |
| Coconut oil | 250-264 |
| Cotton seed oil | 189-198 |
| Soybean oil | 189-195 |
| lard | 190-202 |

#### Iodine Value :

~ 220 – 250

The iodine value of an oil/fat is the number of grams of iodine absorbed

by 100g of the oil/fat, when determined by using Wij’s solution.

The iodine value is a measure of the amount of unsaturation (number of double bonds) in a fat.

R-CH=CH-R + IClexcess == R-CHI-CHCl-R + IClremaining Principle:

The oil/fat sample taken in carbon-tetrachloride is treated with a known excess of iodine monochloride solution in glacial acetic (Wijs solution). The excess of iodine monochloride is treated with potassium iodide and the liberated iodine estimated by titration with sodium thiosulfate solution.

#### Reagents:

1. Potassium dichromate AR
2. Concentrated hydrochloric acid AR
3. Glacial acetic acid, free from ethanol
4. Carbon tetrachloride, analytical reagent grade
5. Iodine mono-chloride (ICl)
6. Potassium iodide - 10% solution prepared fresh
7. Starch solution - Mix 5 g of starch in 30 ml of cold water and slowly pour it with stirring into one litre of boiling water. Boil for three minutes. Allow to cool and decant off the supernatant clear liquid.
8. Wij’s Iodine monochloride solution - Dissolve 10 ml of iodine monochloride in about 1800 ml of glacial acetic acid and shake vigorously. Pipette 5 ml of Wij's solution, add 10 ml of potassium iodide solution and titrate with 0.1N standard sodium thiosulphate solution using starch as indicator. Adjust the volume of the solution till it is approximately 0.2 N. Store in an amber bottle sealed with paraffin until ready for use. Wij’s solutions are sensitive to temp, moisture and light. Store in dark at less than 30°C .
9. Standard sodium thiosulphate solution (0.1N)- Dissolve approximately 24.8 g of sodium thiosulphate crystals (Na2S2O3.5H2O) in distilled water and make up to 1000 ml.

#### Procedure:

Weighout accurately about 0.5-1g of Oil / Fat sample into a 500 ml conical flask with glass stopper, to which 25 ml of carbon tetrachloride have been added. Mix the content well. The weight of the sample shall be such that there is an excess of 50 to 60 percent of Wij’s solution over that actually needed. Pipette 25 ml of Wij's solution and replace the glass stopper after wetting with potassium iodine solution. Shake for proper mixing and keep the flasks in dark for half an hour for non-drying and semi-drying oils and one hour for drying oils.

Carry out a blank simultaneously. After standing, add 15 ml of potassium iodide solution, followed by 100 ml of recently water. Titrate liberated iodine with standardized sodium thiosulphate solution, using starch as indicator at the end until the blue colour formed disappears after thorough shaking with the

stopper on. Conduct blank determinations in the same manner as test sample but without oil/fat.

IClremaining + 2KI == KCl + KI + I2

I2 + starch + 2Na2S2O3 == 2NaI + Na2S4O6

Blue Colourless Iodine value = 12.69 (B – S) N / W

Where, B = volume in ml of standard sodium thiosulphate solution required for the blank.

S = volume in ml of standard sodium thiosulphate solution required for the sample. N = normality of the standard sodium thiosulphate solution.

W = weight in g of the sample.

#### Typical Iodine values

|  |  |  |  |
| --- | --- | --- | --- |
| Coconut oil | 8 – 10 | Cottonseed oil | 100 - 117 |
| Butter | 25 – 40 | Fish oils | 120 - 180 |
| Beef tallow | 30 – 45 | Soybean oil | 125 - 140 |
| Palm oil | 37 - 54 | Safflower oil | 130 - 140 |
| Lard | 45 - 70 | Sunflower oil | 130 - 145 |
| Olive oil | 75 - 95 | Linseed oil | 170 - 205 |
| Peanut oil | 85 - 100 |  |  |

**7. Analysis of Cement**

Cement is a binder, a substance used for construction that sets, hardens, and adheres to other materials to bind them together. **Non-hydraulic cement**, such as slaked lime (calcium oxide mixed with water), hardens by carbonation in the presence of carbon dioxide, which is naturally present in the air. First calcium oxide (lime) is produced from calcium carbonate (limestone or chalk) by calcination at temperatures above 825 °C (1,517 °F) for about 10 hours at atmospheric pressure

CaCO3 ‹ CaO + CO2

The calcium oxide is then *spent* (slaked) mixing it with water to make slaked lime (calcium hydroxide)

CaO + H2O ‹ Ca(OH)2

Once the excess water is completely evaporated (this process is technically called

*setting*), the carbonation starts

Ca(OH)2 + CO2 ‹ CaCO3 + H2O

This reaction takes time, because the partial pressure of carbon dioxide in the air is low. The carbonation reaction requires that the dry cement be exposed to air, so the slaked lime is a non-hydraulic cement and cannot be used under water. This process is called the *lime cycle*. Conversely, **hydraulic cement** hardens by hydration when water is added.

#### Composition

Portland cement consists essentially of compounds of lime (calcium oxide, CaO) mixed with silica (silicon dioxide, SiO2) and alumina (aluminum oxide, Al2O3).

#### Manufacture of Cement

There are four stages in the manufacture of portland cement: (1) crushing and grinding the raw materials, (2) blending the materials in the correct proportions, (3) burning the prepared mix in a kiln, and (4) grinding the burned product, known as “clinker,” together with some 5 percent of gypsum (to control the time of set of the cement).

**Chemical analysis of cement**

The chemical analysis of cement consists of the determination of the following constituents

1. Silica
2. NH4OH group
3. Ferric oxide
4. Alumina
5. Lime
6. Magnesia
7. Sulphide sulphur
8. K2O, Na2O
9. Free calcium oxide in cement and clinker
10. SO3
11. Loss on ignition

#### Determination of Silica:

Transfer 0.5 g of the sample to an evaporating dish, moisten with 10 ml of distilled water, add 5 to 10 ml of hydrochloric acid, and digest with the aid of gentle heat and agitation until the sample is completely dissolved. Evaporate the solution to dryness on a steam-bath. Treat it with 5 to 10 ml of hydrochloric acid and then with an equal amount of water and dish and digest for 10 minutes on the water-bath or hot-plate. Dilute the solution with an equal volume of hot water, immediately filter through an ashless filter paper and wash the separated silica (SiO2) thoroughly with hot water and reserve the residue.

Again evaporate the filtrate to dryness, baking the residue in an oven for one hour at 105 to 110°C. Then treat the residue with 10 to 15 ml of hydrochloric acid. Transfer the residues to a weighed platinum crucible. Dry and ignite the residue at 1100 to 1200°C until the weight remains constant. Treat the ignited residue thus obtained with 1 to 2 ml of distilled water, about 10 ml of hydrofluoric acid and 2 drops of sulphuric acid and evaporate cautiously to dryness. Finally heat the small residue at 1050 to 1100°C for a minute or two; cool and weigh. The difference between this weight and the weight of ignited sample represents the amounts of silica

#### Determination of NH4OH group:

To the filtrate obtained after the removal of silica which shall have a volume of about 200 ml, add a few drops of the methyl red indicator, and heat to boiling, adding a few drops of bromine water or concentrated nitric acid during boiling in order to oxidize any ferrous iron to the ferric condition. Then treat with ammonium hydroxide (1 : 1) drop by drop until the colour of the solution becomes distinctly yellow and smells of ammonia. Bring to boiling the solution containing the precipitates of aluminium and ferric hydroxides and boil for one minute. Allow the precipitate to settle, filter through an ashless filter paper and wash with 2 percent hot ammonium nitrate solution. Place the precipitate in a weighed platinum crucible, ignite to constant weight at 1050 to 1100°C and weigh as combined alumina and ferric oxide.

R2O3 percent = weight of residue × 200

#### Determination of Ferric Oxide

To one gram of the sample, add 40 ml of cold water and, while the mixture is being stirred vigorously, add 15 ml of hydrochloric acid. If necessary, heat the solution and grind the cement. The solution is diluted with distilled water to about 50ml. Heat the contents to boil and add 5% SnCl2 solution (to reduce Fe (III) into Fe (II)) drop wise until yellow colour of Fe (III) disappears. Then cool the solution and add saturated ***HgCl2*** solution until to get a silky white precipitate to oxidize excess SnCl2 if present. Then add 3ml of ortho phosphoric acid, DPA indicator and titrate the total iron against 5/56N ***E2Cr2O7*** solution from the burette until a bluish violet colour appears. Calculate iron as ferric oxide

#### Determination of Alumina:

Dissolve the precipitate obtained in Conc. ***HCl*** and add 15ml of Saturated Solution of Sodium Phosphate and ***NH4OH*** Solution till white precipitate is formed. This precipitate is dissolved in ***HCl***. To the resulting solution 15ml of acetic acid and 10- 15gm of ***sodium thiosulphate*** crystals are added to keep the iron in solution in Ferrous state. The solution is then boiled for 5minutes and ammonium acetate solution is

added. Then aluminum precipitates as ***AlPO4***. Filter the precipitate and ignited at 900oC for 5minutes, cooled and weighed as ***Al2O3***

Percentage of ***Al2O3*** = weight of residue x 0.4178/weight of sample x 100

#### Determination of Calcium oxide (Lime):

The filtrate obtained after Bromine and ***NH4OH*** treatment and separation of iron and aluminium precipitates, it is boiled and then add 5gms of ammonium oxalate is added. The solution is digested for 30 minutes and maintaining the solution alkaline with ***NH4OH***. The precipitate of calcium oxalate formed. Filter off the precipitate and reserve the filtrate for the determination of ***MgO***.

The precipitate is transferred into a beaker and dissolved in dil. ***H2SO4*** solution. Heat the solution gently and titrate the liberated oxalate with a standard ***EMnO4*** solution until permanent pink colour appears. The amount of ***CaO*** can be calculated as,

1ml of 0.1N ***EMnO4*** == 0.0028 gm of ***CaO***

#### EDTA Method:

Take 10 ml of filtrate obtained after the removal of **the determination of Ferric oxide** in a 250-ml concial flask. Add 5 ml of 1 : 1 glycerol with constant stirring and 5 ml of diethylamine. To this add 10 ml of 4N sodium hydroxide solution and shake well to adjust *p*H to highly alkaline range of 12 or slightly more. Add approximately 50 ml of distilled water and 50 mg of solid Patton-Reeder’s indicator. Titrate against

* 1. M EDTA solution to a sharp change in colour from wine red to clear blue 1 ml of 0.01 M EDTA 0.5608 mg of CaO

Calcium Oxide (CaO) percent = 0.05608 × 25 × *V / W*

Where

*V* = Volume of EDTA used in ml, and

*W* = Weight of the sample in g.

#### Determination of MgO:

Estimation of ***MgO*** is based on precipitation Mg as magnesium ammonium phosphate and decomposing as magnesium pyro phosphate.

The filtrate obtained after the removal of calcium, is neutralized with ***HCl*** and made the solution slightly acidic. The solution is diluted to known volume. Then for each 100ml add 20ml of 10% diammonium phosphate ***[(NH4)2HPO4]*** solution is added. The solution is stirred vigorously and add ***NH4OH*** drop wise until the solution is slightly basic. Then magnesium is precipitate as magnesium ammonium phosphate.

The precipitate is allowed to settle for about 5 hours and filtered through filter paper. The precipitate is taken in a porcelain crucible and ignited at about 900oC until a constant weight is obtained. The precipitate decomposes into magnesium pyrophosphate (***Mg2P2O7***). The residue is weighed as ***Mg2P2O7*** from which MgO can be calculated.

***MgO*** = 0.3622 x weight of ***Mg2P2O7***x100

#### Determination of Sulphide sulphur

Place 15 ml of the ammoniacal zinc sulphate solution and 285 ml of water in the beaker. Put 5 g of the sample and 10 ml of water in the flask and shake the flask gently to wet and disperse the cement completely. This step and the following one should be performed rapidly to prevent the setting of the cement. Connect the flask with the funnel and bulb. Add 25 ml of the stannous chloride solution through the funnel and shake the flask. Add 100 ml of hydrochloric acid (1 : 3) through the funnel and shake the flask. During these shakings, keep the funnel closed and the delivery tube in the ammoniacal zinc sulphate solution. Connect the funnel with the source of compressed air, open the funnel, start a slow stream of air, and heat the flask and contents slowly to boiling. Continue the boiling gently for 5 or 6 minutes, cut off the heat, and continue the passage of air for 3 or 5 minutes. Disconnect the delivery tube and leave it in the solution for use as a stirrer. Cool the solution to 20 to 30°C, and 2 ml of the starch solution and 40 ml of hydrochloric acid (1 : 1), and titrate

immediately with the standard potassium iodate solution until a persistent blue colour is obtained.

Sulphur, percent = *EV* × 20

Where

*E* = sulphur equivalent of the potassium iodate solution in g/ml,

*V* = volume in ml of potassium iodate solution required by the sample, and 20 = 100 divided by the weight of sample used (5 g)

#### Determination of SO3:

To one gram of the sample, add 25 ml of cold water, and while the mixture is stirred vigorously add 5 ml of hydrochloric acid. If necessary, heat the solution and grind the material with flattened end of a glass rod until it is evident that the decomposition of the cement is complete. Dilute the solution to 50 ml and digest for 15 minutes at a temperature just below boiling. Filter and wash the residue thoroughly with hot water. Set aside the filter paper with the residue. Dilute the filtrate to 250 ml and heat to boiling. Add slowly drop by drop, 10 ml of hot barium chloride (100 g/l) solution and continue the boiling until the precipitate is well formed. Digest the solution on a steam-bath for 4 hours or preferably overnight. Filter the precipitate and wash the precipitate thoroughly. Place the contents in a weighed platinum crucible ignite at 800 to 900°C, cool in a desiccator and weigh the barium sulphate obtained, calculate the sulphuric anhydride content of the material taken for the test.

SO3 percent = *W* × 34.3

Where *W* = weight of residue (BaSO4) in g; and

34.3 = molecular ratio of SO3 to BaSO4 (0.343), multiplied by 100.

#### Loss on ignition:

Heat 1.00 g of the sample for 15 minutes in a weighed and covered platinum crucible (a porcelain crucible may also be used) of 20 to 25 ml capacity by placing it in a muffle furnace at temperature between 900° and 1000°C; cool and weigh. Check the loss in weight by a second heating for 5 minutes and re-weigh. Record the loss in weight as the loss on ignition and calculate the percentage of loss on ignition to the nearest 0.1. Calculate the percent loss on ignition as below

Percent loss on ignition = loss in weight × 100

#### Determination of free Lime in cement: Ethylene-Glycol Method

The ethylene-glycol method is to be used only for estimating free lime in fresh clinker and freshly ground cement but not with aged cement. Bromocresol green is blue in alkaline solution and changes through green and yellowish green to yellow in acid solution. In aqueous solution, the various colors correspond to the following *p*H values

*p*H

|  |  |
| --- | --- |
| Blue | 5.2 |
| Green | 4.5 |
| Yellow | 3.8 |

Take one gram of cement in a long-necked Pyrex flask of 100 ml capacity and add 50 ml of ethylene glycol. Close the flask with a cork stopper and heat the contents on a water bath for one-half hour to bring calcium oxide into solution. Keep the temperature of the bath between 60 to 70°C and shake the flask vigorously every five minutes to prevent the cement from forming lumps. Alternatively, very pure quartz sand initially washed and thoroughly dried is added to the flask to prevent the cement from baking. More over, the cement-ethylene- glycol mixture is put under the reflux condenser on a water bath at 60 to 70°C. In the event of stubborn cement necessitating a long time to react, the time can be cut-down by adding purest water-free methanol to the ethylene glycol (say 15 cc of former to 30 cc of latter) when on boiling for one- half to one hour under reflux, the solution is ready for titration.

Filter off the solution from the flask quickly using suction, first pouring the clear solution and then the cement on the filter. Wash the cement on filter paper thrice with a 10 ml portion of glycol after filtration. Titrate the filtrate against 0.1 N hydrochloric acid using 3 drops of 1 percent bromocresol green in absolute alcohol as indicator.

# 8. Analysis of Paints

“Paint is defined as a unique homogeneous mixture of three major ingredients namely Binder, Pigment, VOC(Volatile organic compound) & additives, which when applied on the surface as a thin layer that forms a solid dry adherent film after oxidation/evaporation/ polymerisation”.

Paints are variable combinations of Binder, Pigment, Filler/ Extender, Volatile organic compound (Thinner), Driers, Additives (Anti skinning agents, Anti settling agent, Plasticizers, fire retardants etc..)

#### PROPERTIES OF PAINT

* + - It should have high hiding power & the required colour
    - It should be able to resist the atmospheric conditions to which it will be put
    - The films produced should be washable
    - It should resist corrosion
    - The film produced by applying the paint on a surface should have gloss

#### BINDER

**Purpose**

Binds pigment, fillers & additives together and imparts adhesion and strongly influences Glossiness, Durability, Flexibility and Toughness. Binders include resins like Alkyds, Polyurethanes (PU), Epoxy, Polyesters

#### PIGMENTS

* + - “Pigments are finely ground inorganic or organic powders of higher RI (> 1.5),

Higher the RI, more the light is bent & greater the opacity.

* + - Good opacity has good lighting absorbing and / or scattering properties –

Average diameter ranges from 0.01 to 5µ

* + - Widely used pigments: White Lead, Zinc Oxide, Titanium Dioxide, Red Oxide, Carbon Black, Prussian Blue, Chrome Yellow, Aluminium powder etc. ◆ [Titanium dioxide is extensively used because it has good covering power). Titanium is an excellent reflector of infrared light].

Analysis of paints mainly deals with analysis of vehicle and analysis of pigment.

Vehicle consists of thinner or volatile organic compound (VOC). Generally used thinner is oil like turpentine oil, Benzene, Naphtha, Acetone, Carbon tetrachloride and Ethyl alcohol. Analysis of vehicle involves the analysis of oils.

**Analysis of thinner**

Thinners are the liquid used for viscosity adjustment. They are used to dissolve the binder and to facilitate application of paint. Solvents are usually organic liquids or water. Excessive thinner dulls the colour & gloss. Thinners are most hazardous due to their toxicity & flammability. Once the solvent gets evaporated, the remaining paint is fixed on to the surface. The purpose of thinner is to Control flow and application properties.

#### 1. Acid value (Acid Number)

The acid value (*AV) is* the number of milligrams of potassium hydroxide required to neutralize the free acids present in 1 g of an oil sample.

#### Required solutions:

1. Fat or Oil 2. Absolute ethanol alcohol

1. Phenolphthalein 4) 0.1 N KOH

#### Procedure :

Place 5.0 g of fat or oil in a dried conical flask. Add 25 ml of absolute ethanol alcohol and add ( 2-3) drops of phenolphthalein Heat with shaking in water bath for 10 minutes ,then cool and titrate the solution against 0.1 N KOH until pink color appears (end point)

Calculate the acid value (AV) and free fatty acid (%FFA). Acid Value (AV) = mL of KOH x N x 56 / weight of sample

%Free Fatty Acid (FFA) = Acid Value x 0.503 N = Normality of KOH

#### Saponification Value

The saponification value is the number of mg of potassium hydroxide required to neutralize the free acids and to saponify the esters in 1 g of the substance. The saponification number is a measure of the average molecular weight of the triacylglycerols in a sample. Saponification is the process of breaking down a neutral fat into glycerol and fatty acids by treatment with alkali.

Saponification value is a valuable characteristic of oils and fats, which indicates the chain length of the fatty acids present The common vegetable oils exhibit SVs ranging from 160 to 264. SV of mustard oil of about 170-180 is due to the presence of glycerides. 250-264 for coconut oil is indicative of shorter chain acids.

Required Solutions:

1. Fat or Oil
2. 0.5 N alcoholic potassium hydroxide ( alcoholic KOH) prepared by dissolving 30 g potassium hydroxide in 20 mL of water and make the final volume to 1 L using 95 % ethanol. Leave the solution to stand for 24 h before decanting and filtering the solution.
3. 0.5 N Hydrochloric acid
4. Phenolphthalein.

#### Procedure :

Weigh approximately 2 g of the fat or oil into a 250 mL conical flask. Add 25 mL of alcoholic potassium hydroxide solution ( 0.5 N). Attach a reflux condenser and heat the flask contents on a boiling water bath for 1 hour with occasional shaking. While the solution is still hot , add 3 drops of phenolphthalein indicator and titrate the excess potassium hydroxide with the 0.5 N hydrochloric acid ( Vml of hydrochloric acid at end point represents S). Do same above procedure but without sample ( Vml of hydrochloric acid at end point represents B). calculate the saponification number.

Saponification value = 56.1 x (B – S) N / W

Where, B = volume in ml of standard Hydrochloric acid solution required for the blank.

S = volume in ml of standard Hydrochloric acid solution required for the sample. N = normality of the standard sodium Hydrochloric acid solution.

W = weight in g of the sample.

#### Iodine Value :

The iodine value of an oil/fat is the number of grams of iodine absorbed

by 100g of the oil/fat, when determined by using Wij’s solution.

The iodine value is a measure of the amount of unsaturation (number of double bonds) in a fat.

R-CH=CH-R + IClexcess == R-CHI-CHCl-R + IClremaining Principle:

The oil/fat sample taken in carbon-tetrachloride is treated with a known excess of iodine monochloride solution in glacial acetic (Wijs solution). The excess of iodine monochloride is treated with potassium iodide and the liberated iodine estimated by titration with sodium thiosulfate solution.

#### Reagents:

1. Potassium dichromate AR
2. Concentrated hydrochloric acid AR
3. Glacial acetic acid, free from ethanol
4. Iodine mono-chloride (ICl)
5. Potassium iodide - 10% solution prepared fresh
6. Starch solution - Mix 5 g of starch in 30 ml of cold water and slowly pour it with stirring into one litre of boiling water. Boil for three minutes. Allow to cool and decant off the supernatant clear liquid.
7. Wij’s Iodine monochloride solution - Dissolve 10 ml of iodine monochloride in about 1800 ml of glacial acetic acid and shake vigorously. Pipette 5 ml of Wij's solution, add 10 ml of potassium iodide solution and titrate with 0.1N standard sodium thiosulphate solution using starch as indicator. Adjust the volume of the solution till it is approximately 0.2 N. Store in an amber bottle sealed with paraffin until ready for use. Wij’s solutions are sensitive to temp, moisture and light. Store in dark at less than 30°C .
8. Standard sodium thiosulphate solution (0.1N)- Dissolve approximately 24.8 g of sodium thiosulphate crystals (Na2S2O3.5H2O) in distilled water and make up to 1000 ml.

#### Procedure:

Weighout accurately about 0.5-1g of Oil / Fat sample into a 500 ml conical flask with glass stopper, to which 25 ml of carbon tetrachloride have been added. Mix the content well. The weight of the sample shall be such that there is an excess of 50 to 60 percent of Wij’s solution over that actually needed. Pipette 25 ml of Wij's solution and replace the glass stopper after wetting with potassium iodine solution. Shake for proper mixing and keep the flasks in dark for half an hour for non-drying and semi-drying oils and one hour for drying oils.

Carry out a blank simultaneously. After standing, add 15 ml of potassium iodide solution, followed by 100 ml of recently water. Titrate liberated iodine with standardized sodium thiosulphate solution, using starch as indicator at the end until the blue colour formed disappears after thorough shaking with the stopper on. Conduct blank determinations in the same manner as test sample but without oil/fat.

#### IClremaining + 2KI == KCl + KI + I2

**I2 + starch + 2Na2S2O3 == 2NaI + Na2S4O6**

Blue Colourless

Iodine value = 12.69 (B – S) N / W

Where, B = volume in ml of standard sodium thiosulphate solution required for the blank.

S = volume in ml of standard sodium thiosulphate solution required for the sample. N = normality of the standard sodium thiosulphate solution.

W = weight in g of the sample.

## Analysis of pigment

Pigment is the colour imparting material to paints. The analysis of pigment involves mainly determination of BaSO4, total Lead and Lead Chromate.

#### Determination of Barium

Take 1g of sample and dissolve in 100 mL of ethanol. Take 10mL of solution and heat it to boiling, add a slight excess of hot *0.5M sulphuric acid slowly and with constant stirring. Digest on the* steam bath until the precipitate has settled, filter. Dry the crucible and precipitate in an oven at 100-110 °C Weigh as BaS04.

#### Total Lead

Dilute the filtrate from the insoluble material to about 250 cc. and add NH4OH until the solution is slightly alkaline. Then add dil. acetic acid in slight excess. Heat to boiling, and add a hot solution of K2Cr2O7 in excess. Sufficient dichromate solution should be added so that when the PbCrO4 settles, the supernatant liquor is distinctly yellow or orange. Boil until the precipitate settles quickly. Filter through a weighed Gooch crucible. Wash with hot water, dry at 110 C., set the Gooch crucible in a larger platinum crucible, ignite gently, cool in a desiccator and weigh as PbCrO4.

Total Lead

Nearly neutralize the filtrate from the insoluble with NH4OH, and dilute to 350 cc. Pass H2S gas for ten minutes. Cover with a watch glass, place on the steam bath and let settle. Test a portion of the clear liquid for complete precipitation by diluting with an equal volume of water and passing in more H2S. If precipitation is not complete, dilute the whole to about 500 cc. and pass in more H2S. Finally filter out the PbS and wash rapidly with water containing a little H2S. Dissolve the PbS with hot cone. HNO3 containing a little bromine water, dilute to about 100 cc., filter out sulfur if necessary, cool, add 5 cc. of cone. H2SO4 and evaporate to strong SO3 fumes. Cool and add 100 cc. of water and 50 cc. of alcohol. Let stand one hour or until the PbSO4 settles clear. Filter on a weighed Gooch crucible, wash with 5% H2SO4 and finally with alcohol, dry at 105 C., set the crucible in a larger platinum crucible, ignite until pure white, cool and weigh as PbSO4.

#### Lead Chromate

Add a slight excess of clear lead acetate solution (a basic solution can generally be cleared up by adding a few drops of acetic acid), digest on the steam bath until the precipitate settles clear, and filter on a weighed Gooch crucible, washing with hot water; dry. set the crucible inside of a larger platinum crucible, ignite gently, cool in a desiccator and weigh as PbCrO4 . The precipitate should not be allowed to stand in the beaker an undue length of time after settling clear on account of the danger of becoming basic, nor should the solution be boiling when the lead acetate is added or at any time after.

# 9. Analysis of Phosphate rock

Worldwide, most soils and crops require phosphorus (P) additions to improve fertility and production. Directly applying unprocessed phosphate rock to soil may provide a valuable source of plant nutrients in specific conditions. **Phosphorite, phosphate rock** or **rock phosphate** is a non-detrital sedimentary rock which contains high amounts of phosphate minerals. The phosphate content of phosphorite (or grade of phosphate rock) varies greatly, from 4% to 20% phosphorus pentoxide (P2O5). For general use in the fertilizer industry, phosphate rock or its concentrates preferably have levels of 30% phosphorus pentoxide (P2O5), reasonable amounts of calcium carbonate (5%), and <4% combined iron and aluminium oxides. Worldwide, the resources of high-grade ore are declining, and the beneficiation of lower grade ores by washing, flotation and calcining is becoming more widespread. In addition to phosphate fertilisers for agriculture, phosphorus from rock phosphate is also used in animal feed supplements, food preservatives, anti-corrosion agents, cosmetics, fungicides, ceramics, water treatment and metallurgy.

#### Loss on ignition

1gm of sample is taken in a platinum crucible and ignited at 950-1000oC for 30minutes. The ignited sample is cooled in a desiccator and weighed. The loss in weight will represent the loss on ignition

#### Determination of Moisture

Place 5.00 g of sample in a glass-stoppered weighing bottle. Dry for 1 hour at 105° C in a well-ventilated oven. At the end of 1 hour, loosely stopper the bottle, and cool in a desiccator. Momentarily raise the stopper, again put it in place, and weigh. The loss in weight is regarded as moisture.

#### Determination of Phosphorus Pentoxide

Phosphorus is directly precipitated as magnesium-ammonium-phosphate in presence of ammonium citrate, ignited and weighed as magnesium pyrophosphate. Transfer 0.5 g of a sample into a flask and add 15 ml of concentrated hydrochloric acid and 3 ml of concentrated nitric acid and boil gently for 30 minutes. Then add 30 g

of ammonium citrate, 10 ml of concentrated hydrochloric acid, and 100 ml of magnesia mixture. Neutralize the solution with concentrated ammonium hydroxide. Using litmus paper as indicator, and add 3 ml of concentrated ammonium hydroxide in excess. Dilute the solution to 225 to 250 ml with water, shake vigorously for about one and half hour, and allow standing overnight. Filter through a paper and discard the filtrate. Transfer the paper and precipitate to a weighed silica or porcelain crucible. Char the paper without flaming, burn off the carbon below 900°C and finally ignite to **a** constant mass, preferably in a muffle, at 1050 to 1100°C.

#### %P2O5 = Wt. of the ppt x 63.78 / wt. of the sample

1. **Determination of CaO:**

Transfer 0.5 g of the sample to a 400-ml beaker. Dissolve, by boiling gently with 20 ml of concentrated hydrochloric acid and 10 ml of concentrated nitric acid, until the volume is reduced to about 10 ml. Dilute to 100ml and add sufficient amount of ammonium chloride to hold magnesium in the solution and boil the solution. Then add 5gms of ammonium oxalate. The solution is digested for 30 minutes and maintaining the solution alkaline with ***NH4OH***. The precipitate of calcium oxalate formed. Filter off the precipitate. The precipitate is transferred into a beaker and dissolved in dil. ***H2SO4*** solution. Heat the solution gently and titrate the liberated oxalate with a standard ***EMnO4*** solution until permanent pink colour appears. The amount of ***CaO*** can be calculated as,

1ml of 0.1N ***EMnO4*** == 0.0028 gm of ***CaO***

#### Determination Of Fluorine By Distillation Method

Transfer 0.5 g of an accurately weighed sample to a 250-ml distillation flask containing 0.5 g of sodium silicate. Add 10 ml of perchloric acid. Place a 1000ml flask under the condenser. Connect the distillation flask to the condenser and distil the solution until the boiling point reaches 140°C. While this is being done heat the water in the steam generator to boiling but do not allow the steam to get in the flask*.* When the temperature reaches 1400C, admit steam into the flask. Maintain the temperature at

140°C by adjusting the steam flow and heating of the flask*.* Continue distillation and make the volume up to the mark and mix well. Pipette out 50-ml aliquot into a 250-ml

beaker. Add 50 ml of water, 10 drops of sodium alizarine sulphonate indicator solution and mix. Add sodium hydroxide solution slowly with stirring till the solution becomes pink. Add dilute hydrochloric acid drop by drop with stirring till the pink colour is just discharged leaving the solution just acid. Add two millilitres of buffer solution and titrate with standard thorium nitrate solution with constant stirring, till a permanent pink end point is reached. The colour intensity at the end point should be kept in mind and the titration should be stopped exactly at the same colour intensity for both the standard thorium nitrate solution and the test solution titration.

#### Determination Of Carbon Dioxide

Transfer 1 g of an accurately weighed sample to the flask and cover it with water. Insert the stopper carrying the separatory funnel and a condenser***.*** Pass air that is free from carbon dioxide through the system until it is judged that all carbon dioxide has been removed. Close the stop-cock in the separatory funnel, and insert the weighed absorption bulbs. Half fill the separatory funnel with dilute hydrochloric acid, replace the stopper carrying the air, and see that there is free passage for gases through the train. Open the stop-cock in the separatory funnel and run acid into the flask slowly if there is much carbon dioxide, and rapidly if there is but little. When it is judged that carbon dioxide has been boiled out of the solution, remove the flame, increase the current of air and sweep out all carbon dioxide. Disconnect the weighed bulbs, close the inlet and outlet tubes, and place them on the balance case. When cool, open the stopper momentarily and weigh.

#### Determination of Ferric Oxide

Transfer 0.5 g of the sample to a 400-ml beaker. Dissolve, by boiling gently with 20 ml of concentrated hydrochloric acid and 10 ml of concentrated nitric acid, until the volume is reduced to about 10 ml. Heat the contents to boil and add 5% SnCl2 solution (to reduce Fe (III) into Fe (II)) drop wise until yellow colour of Fe (III) disappears. Then cool the solution and add saturated ***HgCl2*** solution until to get a silky white precipitate to oxidize excess SnCl2 if present. Then add 3ml of ortho phosphoric acid, DPA indicator and titrate the total iron against 5/56N ***E2Cr2O7*** solution from the burette until a bluish violet colour appears. Calculate iron as ferric oxide

#### Determination of Alumina

Transfer 0.5 g of the sample to a 400-ml beaker. Dissolve, by boiling gently with 20 ml of concentrated hydrochloric acid and 10 ml of concentrated nitric acid, until the volume is reduced to about 10 ml. Then add 15ml of Saturated Solution of Sodium Phosphate and ***NH4OH*** Solution till white precipitate is formed. This precipitate is dissolved in ***HCl***. To the resulting solution 15ml of acetic acid and 10- 15gm of ***sodium thiosulphate*** crystals are added to keep the iron in solution in Ferrous state. The solution is then boiled for 5minutes and ammonium acetate solution is added. Then aluminum precipitates as ***AlPO4***. Filter the precipitate and ignited at 900oC for 5minutes, cooled and weighed as ***Al2O3***

Percentage of ***Al2O3*** = weight of residue x 0.4178/weight of sample x 100

#### Determination of Silica

Transfer 0.5 g of the sample to an evaporating dish, add 5 to 10 ml of hydrochloric acid, and digest with the aid of gentle heat and agitation until the sample is completely dissolved. Evaporate the solution to dryness on a steam-bath. Treat it with 5 to 10 ml of hydrochloric acid and then with an equal amount of water and dish and digest for 10 minutes on the water-bath or hot-plate. Dilute the solution with an equal volume of hot water, immediately filter through an ashless filter paper and wash the separated silica (SiO2) thoroughly with hot water and reserve the residue.

Again evaporate the filtrate to dryness, baking the residue in an oven for one hour at 105 to 110°C. Then treat the residue with 10 to 15 ml of hydrochloric acid. Transfer the residues to a weighed platinum crucible. Dry and ignite the residue at 1100 to 1200°C until the weight remains constant. Treat the ignited residue thus obtained with 1 to 2 ml of distilled water, about 10 ml of hydrofluoric acid and 2 drops of sulphuric acid and evaporate cautiously to dryness. Finally heat the small residue at 1050 to 1100°C for a minute or two; cool and weigh. The difference between this weight and the weight of ignited sample represents the amounts of silica.

#### Determination Of Manganese Oxide

Transfer 0.500 g of sample to a 300-ml Erlenmeyer flask and add 5 ml of nitric acid and 15 ml of 60-percent perchloric acid. Heat to boiling, and continue the boiling until fumes of perchloric acid begin to be evolved. Remove from the source of heat, cool somewhat, and add 10 ml of diluted hydrochloric acid (1+1). Now boil the solution until most of the perchloric acid has been volatilized. Reduction of the volume to about 5 ml is satisfactory. Cool the solution and add 50 ml of warm diluted nitric acid in which 0.5 g of boric acid has been dissolved. Digest for a few minutes, cool, filter through a paper of loose texture, and wash the flask and paper a few times with warm water. To the filtrate and washings in a 300-ml Erlenmeyer flask add 5 ml of 85-percent phosphoric acid and 0.5 to 1.0 g of potassium periodate. Boil for 10 minutes, cool, dilute if necessary, and determine the amount of manganese in the solution by comparing the color with that obtained by dissolving and similarly treating a material of known manganese content.

#### Determination of sulphur:

To determine the sulphur, weigh 1g of ore sample and transfer into beaker. Add a mixture of 40ml of ***HNO3*** and 5ml of ***HCl*** and heat in a fume chamber for 5ml liquid remains in the beaker. Add a pinch of pure ***Na2CO3*** (to fix the Sulphate formed by aqua regia in the form of ***Na2SO4***) and evaporate to dryness. Cool the residue and dissolve in 25ml of Conc.***HCl*** and dilute to 50ml. Then remove all the ***iron*** by adding an excess of ammonia solution as ***Fe(OH)3***. Neutralize the filtrate with ***HCl*** , boil the solution and add 100 ml of ***BaCl2*** solution. Stir vigorously and allowed to stand for 30min. filter the precipitate and dry until constant weight is obtained. The precipitate is weighed as ***BaSO4***.

Percentage of sulphur = weight of ***BaSO4***x 0.1374x100

#### Determination of MgO:

Estimation of ***MgO*** is based on precipitation Mg as magnesium ammonium phosphate and decomposing as magnesium pyro phosphate.

Transfer 0.5 g of the sample to an evaporating dish, add 5 to 10 ml of hydrochloric acid, and digest with the aid of gentle heat and agitation until the sample is completely dissolved. The solution is diluted to known volume. Then for each 100ml add 20ml of 10% diammonium phosphate ***[(NH4)2HPO4]*** solution is added. The solution is stirred vigorously and add ***NH4OH*** drop wise until the solution is slightly basic. Then magnesium is precipitate as magnesium ammonium phosphate. The precipitate is allowed to settle for about 5 hours and filtered through filter paper. The precipitate is taken in a porcelain crucible and ignited at about 900oC until a

constant weight is obtained. The precipitate decomposes into magnesium pyrophosphate (***Mg2P2O7***). The residue is weighed as ***Mg2P2O7*** from which MgO can be calculated.

***MgO*** = 0.3622 x weight of ***Mg2P2O7***x100

#### Determination of Alkali

5g of phosphate rock is dissolved in HCl and few drops of ***HNO3*** and evaporate to dryness. The dried mass is redissolved in 15ml of ***HCl*** and 30ml of water. The insoluble residue is ignited in a platinum crucible and treated with ***H2SO4*** and sufficient HF to decompose silicates and dissolve the residue in water. The solution is added to previous filtrate. Then add ***BaCl2*** solution and filter off ***BaSO4***. ***BaCl2*** transforms alkali sulphates into chlorides. The filtrate is heated and added an excess of ammonium carbonate solution. The filtrate is evaporated to dryness and weighed as mixture of ***ECl*** and ***NaCl***.

To the residue a little water is added to dissolve and then platinic chloride and equal amount of alcohol are added. Then a residue of potassium platinic chloride ***(E2[PtCl6]*** will separate out. Filter off the crystals, dry at 120oC and weigh.

#### Sampling:

1. **Analysis of Soils**

Sampling is an important step of any analysis. For cereals, vegetables, grasses and herbs the samples should be drawn from 0-15 cm depth. For plantation crops, trees and shrubs prepare composite sample from soil collected at depth of 0-30, 30-60 and 60-100 cm from 4 to 5 pits in about 0.5 ha field. The field sample is spread out on a tray for air drying. When it dries, sieve over a 2 mm sieve and store in an air tight polythene bag/glass / PVC/ porcelain jar. The sampling strategy may vary depending upon the shape of the land and intended purpose.

#### Sample Preparation for Elemental Analysis

For the release of mineral elements from soil and sediments, wet oxidation of sample is carried out. Wet oxidation employs oxidizing acids like HNO3- HClO4-HF tri acid mixture or HNO3-HClO4 di-acid mixture. Use of HClO4 avoids the volatilization loss of K and provides a clear solution while HF helps removing silica.

#### HNO3/HClO4 Digestion

Weigh 0.5-1.0 g sample of air dried soil in digestion tube and add 3 ml conc. HNO3 digest on electrically heated block for 1 h at 145oC. Then add 4 ml of HClO4 and heat it to 240o C for to further one hour. Cool and filter through Whatman # 42 filter paper and makeup to 50 ml volume. Determine P, K, Na, Ca, Mg, Al, B, Fe, Mn, Cu, Zn, Cd, Ca, Ni, Pb, Co, Mo, Si, Ti, Sr, V, and Ba by ICP-AES or ICP-MS or AAS.

#### Determination of Moisture:

Place a porcelain crucible in the oven at a temperature of 1050 C and leave it for 2 hours. Then cool it down to room temperature in a desiccator. Weigh the empty crucible (Empty Crucible weight =A). Weigh at least 10g of sample in the crucible and weigh it again (Sample + Crucible weight =B). Place the crucible at least 12 hours

in the oven at 1050 C. Then cool it down to room temperature in a desiccator and weigh again (C ).

##### Calculation

M (moisture content) % = (B-C)**/**(C-A) x 100%

#### Determination of Total Nitrogen (Kjeldhal method)

##### Reagents

* Digestion catalyst: Mixture of K2SO4/ Na2SO4 and Se (5 g:5 mg respectively).
* 40 % Sodium hydroxide: Dissolve 400 g of NaOH in distilled water and make volume up to one litre.
* 2% Boric acid: Dissolve 20 g of H3BO3 power in warm distilled water and dilute to one litre.
* Mixed indicator: Dissolve 70 mg of methyl red and 100 mg of bromocresol green in 100 ml of ethyl alcohol. Add 10 ml of this mixed indicator to each litre of 2% boric acid solution and adjust the pH to 4.5 with dil. HCl or dil. NaOH.
* 0.01N Sulphuric acid: Prepare approximately 0.1N H2SO4 by adding 2.8 ml of conc. H2SO4 to about 990 ml of distilled water. Standardize it against 0.1 N standard
* NaOH solution. Dilute 10 times this 0.1N H2SO4 to get strength of 0.01 N.

#### Procedure

* Weigh 5 g of sample into digestion tube and moist it with distilled water.
* Add 20 ml of conc. H2SO4 and 5 g of catalyst and place the tube in digestion unit.
* Turn the heating equipment to about 4000C and continue heating till the mixture is transparent and allow it to cool.
* Add 40% NaOH in digest till the colour change blackish and then distilled it. Collect the distillate (librated ammonia) into 10 ml of 2% boric acid solution.
* Titrate the distillate against 0.01N H2SO4 solution until pink colour starts appearing.
* Run a blank without soil for each set of samples.

##### Calculation



* Where
* S= Volume of acid used against sample.
* B= Volume of acid used against blank.
* N= Normality of acid.

#### Determination of Total Phosphorous

Phosphorus in soil and sediments can be determined in the acid digest by Vanadomolybdophosphoric yellow colour method. Ammonium molybdate reacts under acidic conditions to form a heteropoly acid and molybdophosphoric acid. In the presence of vanadium, yellow vanadomolybdophosphoric acid is formed. The intensity of the yellow colour is proportional to phosphate concentration.

#### Reagents

* + 1. Solution A: Dissolve 25 g of ammonium molybdate in 300 ml warm distilled water and cool it.

1. Solution B: Dissolve 1.25 g of ammonium metavandate in 300 ml boiled distilled water. Cool and add 250 ml conc. HNO3. Cool solution B and mix with solution A and make up to one litre.
2. Standard P solution: Dissolve 0.2195 g of dried KH2PO4 in distilled water, acidify with 25 ml of 7N H2SO4 and make the volume up to one litre to get 50 mg/L P solution.

#### Procedure

Place 10 ml of acid digests of soil sample in a 50 ml volumetric flask, add 10 ml of the vanadate-molybdate reagent and dilute to 50 ml. Mix well and read the P concentration after 10 minutes using spectrophotometer at 420 nm. Take 0, 1, 2, 3, 4 and 5 ml of the 100 mg/l P solution in 50 ml volumetric flask and develop colour in identical manner. Calibrate the spectrophotometer with known P concentration and read the concentration of sample.

#### Determination of Silica:

Take 5g of finely ground soil and mix it with about 3-4 g of sodium Carbonate in a nickel crucible. Fuse the contents by slow heating for 10-15minutes and cool. Add 2g more of sodium Carbonate and fuse again about 10minutes. Extract the fused mass into a beaker containing 300ml of water. The silica will be converted into sodium silicate. Extract the fused mass with water and add excess of dil.HCl and evaporate to dryness and redissolve in dil.HCl and filter. Dry the residue and weigh as SiO2. The residue may be treated further with dil.H2SO4 and HF which gives the more precise result of SiO2.

#### Determination of Lime(CaO)

The filtrate obtained after the removal of Silica is boiled and then add 5gms of ammonium oxalate is added. The solution is digested for 30 minutes and maintaining the solution alkaline with ***NH4OH***. The precipitate of calcium oxalate formed. Filter off the precipite.

The precipitate is transferred into a beaker and dissolved in dil. ***H2SO4*** solution. Heat the solution gently and titrate the liberated oxalate with a standard ***EMnO4*** solution until permanent pink colour appears. The amount of ***CaO*** can be calculated as,

1ml of 0.1N ***EMnO4*** == 0.014 gm of ***CaO***

#### Determination of total Alkali

These are important elements because on their effect on the physico-chemical behavior of the soil and the role they in the plant nutrition. These alkali elements can be estimated by either AAS or Flame photometer. Sodium can be determined by AAS at 589nm light and Potassium can be determined by AAS at 766.5nm light using Air- Propane flame.



#### Soil absorption ratio

The Soil absorption ratio is an irrigation water quality parameter used in the management of sodium affected soils. It is an indicator of the suitability of water for use in agricultural irrigation.

SAR =

SAR allows assessment of the state of flocculation in a soil. Sodium and Potassium ions facilitate the dispersion of clay particles while Calcium and Magnesium promote their flocculation.

In general , the higher the sodium absorption ratio , the less suitable the water is for irrigation.

# 11. Analysis of Fertilizer

Any material applied to a soil or plant to supply essential elements is called Fertilizer

What are some different types of fertilizer?

1. Mineral
2. Organic
3. Inorganic

#### Mineral Fertilizer

* + Simply ground rocks containing nutrients
  + Example: Dolomite lime provides calcium and magnesium
  + Usefulness is limited as they dissolve very slowly

#### Organic Fertilizers

* + Crop Rotation
  + Animal Manures
  + Sewage Sludge
  + Septage
  + Compost :Municipal, food processing and industrial organic residues; usually dumped in landfills and ocean; much potential for composting
  + Peat :Partly decayed vegetable matter

#### Description of Inorganic

* + Chemical fertilizers
  + Made by industry
  + Some are mined, others completely manufactured
  + High nutrient content, therefore less expensive

#### Typical examples of Fertilizers: Nitrogen Fertilizers

* Ammonium Sulfate
* Anhyd. Ammonia
* Urea
* Nitrate of Soda
* Ammonium Phosphorus
* Calcium Cynamide

#### Common Phosphorus Fertilizers

* Di-Ammonium Phosphate
* Superphosphate (16-20%)
* MonoAmmonium Phosphate
* Bone Meal - made from grinding bones
* Manure

#### Potassium Fertilizers

* Muriate of potash (KCl) -60% potash, accounts for 97% of all potassium fertilizers
* Costs less and dissolves easily in water
* Nitrate of potash (KNO3) -44% potash and 13% Nitrogen, common for container plants

percent content.

**Analysis of Fertilizer**

Analysis of fertilizer means finding the elements in the bag and their

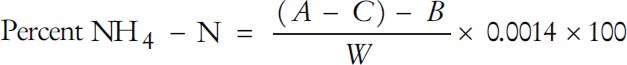
1. **Determination of Ammonical nitrogen Kjeldahl method**

This test method is applicable to fertilizers containing no nitrate nitrogen.

Weigh 0.5 g -5 g of fertilizer sample and put it in a 300-mL-500-mL digestion flask. Add 5 g -10 g of catalyst (K2SO4 + CuSO4,) and further add 20 mL -40 mL of

Hydrochloric acid, shake to mix and heat gently. After bubbles cease to form, heat until white smoke of hydrochloric acid evolves. Ignite until organic matters are completely digested. After standing to cool, add a small amount of water, mix well by shaking, transfer to a 250-mL -500-mL volumetric flask with water and further mix by shaking. After standing to cool, add water up to the marked line to make the digestion solution.

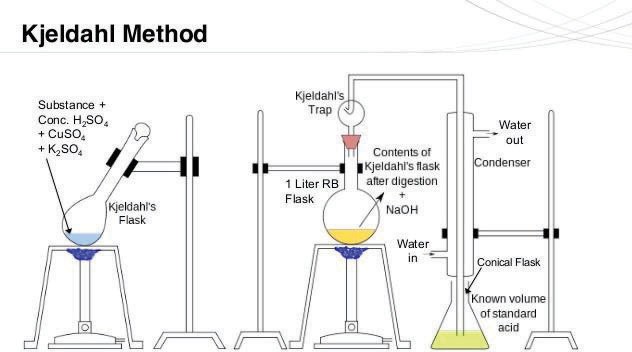
Transfer a predetermined amount of the digestion solution to a 300-mL distillation flask, add a proper amount of sodium hydroxide solution (200 g/L -500 g/L),and immediately connect this distillation flask to the steam distillation apparatus. Send steam to the distillation flask to heat the solution in the distillation flask, and distill at a distillation rate of 5mL/min-7 mL/min. Stop distilling when the distillate has reached 120mL -160 mL. Wash the part of the steam distillation apparatus that came in contact with the solution in the acceptor with a small amount of water, and pool the washing with the distillate.Titrate the distillate with 0.1 mol/L -0.2 mol/L sodium hydroxide solution until the color of the solution becomes pink.



* where:
* *A* = ml of standard acid (0.1M HCl) taken to receive ammonia;
* *B* = ml of standard alkali (0.1M NaOH) used in titration;
* *W* = weight of the sample taken;
* *C* = ml of standard alkali used in the blank.
* 1 ml 0.1M HCl = 0.0014 g N

1. **Determination of Ammoniacal plus nitrate-nitrogen by the distillation method**

Devarda’s alloy (50 percent Cu, 45 percent Al, and 5 percent Zn) reduces NO3 to NH4 in an alkaline condition. The method is same as for NH4-N estimation (above), except that 2-3 g of Devarda’s alloy is added before distillation in order to take into account the NO3 by reducing it to ammonia form.



### Determination of Phosphorous

Phosphate is generally present as bound with Ca as monocalcium phosphate, dicalcium phosphate and tricalcium phosphate.

Monocalcium phosphate is in water soluble form, is considered available, while dicalcium phosphate becomes available in slightly acidic situations. Tricalcium phosphate is in an unavailable form and can be available only in acidic situations.

Pipette 5-–25 ml of aliquot (sample solution) depending on the P content in a 250 ml beaker, and dilute to 100 ml with distilled water. Add about 5–-10 ml of concentrated HNO3 and about 10 g of ammonium nitrate. Heat this mixture on a water-bath at 55-– 60 °C for 10 minutes. Add 3 percent ammonium molybdate solution in the beaker drop by drop with the help of a burette. Continue stirring with a glass rod until about 50 ml of molybdate solution is added. Stir for another few minutes until the yellow precipitate appears to become granular. Cover the beaker with glass and allow it to

settle for some time. Decant the clear solution through No. 44 filter paper, and wash the precipitate with 2 percent sodium nitrate solution, agitate thoroughly, and allow the precipitate to settle.

Transfer the precipitate to the filter paper, and wash with NaNO3 solution until free from acid (by test with a litmus paper). Transfer the precipitate and filter paper to a beaker, and add 10 ml of 0.1M NaOH at a time by pipette until the precipitate becomes soluble. Add 1-–2 drops of 1 percent phenolphthalein, and titrate the excess of alkali against 0.1M sulphuric acid. Run a reagent blank with each batch.

* The calculation is as follows: 23 g equivalent of NaOH = 31 g P = 71 g P2O5 (P

× 2.29 = P2O5)

### Determination of Potassium

In all potassium fertilizers, K is generally present in water-soluble form. Therefore, it is estimated directly in fertilizer solution either gravimetrically, volumetrically or flame photometrically. In manures and organic fertilizers, wet digestion with acid is required prior to determination of K in order to bring the element into solution by digestion.

#### STPB method

Potassium from the fertilizer sample is first extracted with water or ammonium oxalate. The K in extracted solution is precipitated with an excess of STPB as potassium tetraphenyl boron. The excess of STPB is backtitrated with benzalkonium chloride (BAC) or quaternary ammonium chloride using Clayton yellow as indicator:

#### Procedure:

Extraction/preparation of sample solution: Dissolve a known weight (2.5 g) of straight K fertilizer in 200 ml of distilled water, and make the volume up to 250 ml for estimation. For NPK complex fertilizers or NPK fertilizer mixtures, dissolve the sample in 125 ml of water, add 50 ml of 4 percent ammonium oxalate solution, and boil for 30 minutes; after cooling, filter through dry No. 12 filter paper, and make the

volume up to 250 ml for further estimation. Transfer 15 ml of aliquot of sample solution to a 100 ml volumetric flask and add 2 ml of 20 percent NaOH and 5 ml of HCHO.

Add 1 ml of standard STPB solution for each 1 percent of K2O expected in the sample plus an additional 8 ml in excess in order to ensure complete precipitation. Dilute to volume (100 ml) with water, mix thoroughly, let it stand for 5–-10 minutes, and pass it through No. 12 filter paper (or equivalent). Transfer 50 ml of filtrate to a 250 ml Erlenmeyer flask, add 6-–8 drops of Clayton yellow indicator, and titrate excess STPB with standard BAC solution to pink end point.

#### The calculation is:



where, *f* = % K2O/ml of STPB solution. This factor applies to all fertilizers where 2.5 g of sample is diluted to 250 ml, and 15 ml of aliquot is taken for analysis. To express the results as K rather than K2O, substitute 28.73 for 34.61 in calculating the value of *f*.

When the solution containing a suitable compound of the metal atom to be determined is aspirated into a flame, the following steps may occur: Evaporation of solvent, leaving the solid residue. Vapourisation of the solid with dissociation into its constituent atoms, initially in the ground state. These neutral atoms are excited by the thermal energy of the flame. The excited atoms which are unstable emit characteristic radiation and return to lower energy state. If we measure the extent of emitted radiation forms the basis of Flame Photometry or Flame emission spectroscopy

A calibration curve for use in flame emission spectrometry measurements is plotted by aspirating into the flame samples of solutions containing known concentrations of the element to be determined, measuring the emission of each solution, and then constructing a graph in which the measured emission is plotted against the concentration of the solutions.

# 12. Analysis of Fuels

A fuel is a combustible substance containing carbon as the main constituent which on proper burning gives large amount of heat that can be used economically for domestic and industrial purposes. During the process of combustion of a fuel, the atoms of carbon, hydrogen, etc combine with oxygen with simultaneous liberation of heat.

So, carbon compounds have been used for many centuries as the source of heat and energy.

The main source of fuel is coal and petroleum. These are stored fuels available in earth's crust and are generally called fossil fuels because they were formed from the fossilised remains of plants and animals.

#### Classification of Fuels

1. **Primary fuels** which occur in nature as such, e.g. coal, petroleum and natural gas.
2. **Secondary fuels** which are **derived from the primary fuels**, e.g. coke, gasoline, coal gas, etc.

Both primary and secondary fuels may be further classified based upon their physical state as

(i) solid fuels (ii) liquid fuels and (iii) gaseous fuels

#### Coal:

Coal is regarded as a fossil fuel produced from large accumulations of vegetable debris due to partial decay and alteration by the action of heat and pressure over millions of years. Coal is a highly carbonaceous matter that has been formed as a result of alteration of vegetable matter (e.g., plants) under certain favourable conditions. It is chiefly composed of C, H, N, and O, besides non-combustible inorganic matter.

In order to assess the quality of coal the following two types of analysis are made.

1. **Proximate Analysis** It includes the determination of moisture, volatile matter, ash and fixed carbon. This gives quick and valuable information regarding commercial classification and determination of suitability for a particular industrial use.
2. **Fltimate Analysis** It includes the determination of carbon, hydrogen, nitrogen, sulphur and oxygen in coal. Since it is used for the determination of elements present in the coal, it is also called elemental analysis. This analysis gives exact results and are useful in calculating the calorific value of coal using Dulong's formula.

**Proximate analysis of Coal**

1. **Determination of Moisture**: About 1 g of finely powered air-dried coal sample is weighed in a crucible. The crucible is placed inside an electric hot air-oven, maintained at 105° - 110°C. The crucible is allowed to remain in oven for 1 hour and then taken out, cooled in a desiccator and weighed. Loss in weight is reported as moisture (on percentage-basis).

Percentage of moisture = Loss in weight x 100

Wt. of coal taken

#### Determination of Volatile matter:

The dried sample of coal left in the determination of moisture is taken and the crucible is then covered with a lid and placed in an electric furnace (muffle furnace), maintained at 925°± 20°C. The crucible is taken out of the oven after 7 minutes of heating. The crucible is cooled first in air, then inside a desiccator and weighed again. Loss in weight is reported as volatile matter on percentage-basis.

**Percentage of volatile matter= Loss in weight due to removal of volatile matter x 100**

**Wt. of coal sample taken**

#### Determination of Ash:

The residual coal in the crucible after moisture determination is then heated without lid in a muffle furnace at 700 ± 50° C for 1/2 *hour.* The crucible is then taken out, cooled first in air, then in desiccator and weighed. Heating, cooling and weighing is repeated, till a constant weight is obtained. The residue is reported as ash on percentage-basis.

Percentage of ash = Wt. of ash left x 100

Wt. of coal taken

#### Determination of Fixed carbon:

Percentage of fixed carbon = 100 - % of (moisture + volatile matter + ash) high percentage of fixed carbon is desirable.

### Importance of proximate analysis

Proximate analysis provides following valuable information in assessing the

*quality of coal:*

1. **Moisture:** Moisture lowers the effective calorific value of coal. Moreover, it quenches the fire in the furnace. Hence, lesser the moisture content, better the quality of coal as a fuel. However, presence of moisture, up to 10%, produces a more uniform fuel-bed and less of "fly-ash".
2. **Volatile matter**: A high volatile matter containing coal burns with a long flame, high smoke and has low calorific value. Hence, lesser the volatile matter, better the rank of the coal. Higher volatile content in coal is undesirable.

A high volatile matter content means that high-proportion of fuel will be distilled and burned as a gas or vapour. The volatile matter present in the coal may be combustible gases (such as methane, hydrogen, carbon monoxide and other hydrocarbons) or non-combustible gases (like CO2 and N2). Volatile matter content is of special significance in coal gas manufacture and in carbonization

plants, particularly when by-product recovery is the main object. Thus, high- volatile matter containing coals do not take well; whereas medium-volatile matter content coals are capable of yielding hard and strong coke on carbonization.

1. **Ash** is a useless, non-combustible matter, which reduces the calorific value of coal. Moreover, ash causes the hindrance to the flow of air and heat, thereby lowering the temperature. Also, it often causes. trouble during firing by forming clinker. This in-turn causes obstruction to air supply; thereby the burning of coal becomes *irregular.* Hence, lower the ash content, better the quality of coal. The presence of ash also increases transporting, handling and storage costs. The presence of ash also causes early wear of furnace walls, burning of apparatus and *feeding* mechanism*.*
2. **Fixed carbon**: Higher the percentage of fixed carbon, greater is its calorific and better the quality coal. Greater the percentage of fixed carbon, smaller is the percentage of volatile matter. This also represents the quantity of carbon (in coal) that can be burnt by a primary current of air drawn through the hot bed of a fuel.

### Fltimate Analysis of Fuels

#### Determination of Carbon and hydrogen:

About 1-2 g of accurately weighed coal sample is burnt in a current of oxygen in a combustion apparatus. C and H of the coal are converted into CO2 and H2O respectively. The gaseous products of combustion are absorbed respectively in KOH and CaCl2 tubes of known weights. The increase in weights of these are then determined.

Percentage of C = Increase in weight of KOH tube x 12 x 100

Weight of coal sample taken x 44 Percentage of H = Increase in weight of CaCl2 tube x 2 x 100

Weight of coal sample taken x 18

#### Determination of Nitrogen:

About 1 g of accurately weighed powdered 'coal is heated with concentrated H2SO4 along-with K2SO4(catalyst) in a long-necked flask(called Kjeldahl's flask). After the solution becomes clear, it is treated with excess of KOH and the liberated ammonia is distilled over and absorbed in a known volume of standard acid solution. The unused acid is then determined by back titration with standard NaOH solution. From the volume of acid used by ammonia liberated, the percentage of N in coal is calculated as follows:

Percentage of N = Volume of acid used x Normality x 1.4

Weight of coal taken

**Nitrogen** has no calorific value and hence, its presence in coal is undesirable; thus, a good quality coal should have very little nitrogen content.

#### Determination of Sulphur :

It is determined from the washings obtained from the known mass of coal, used in a bomb calorimeter for determination of a calorific value. During this determination, S is converted into sulphate. The washings are treated with barium chloride solution, when barium sulphate is precipitated. This precipitate is filtered, washed and heated to constant weight.

Percentage of S = Weight of BaSO4 obtained x 32 x 100

Weight of coal sample taken in bomb x 233

**Sulphur**, although contributes to the heating value of coal, yet on combustion produces acids (SO2 and SO3), which have harmful effects of corroding the equipments and also cause atmospheric pollution. Sulphur is, usually, present to the extent of 0.5 to 3.0% and derived from ores like iron pyrites, gypsum, etc., mines along-with the coal.

Presence of sulphur is highly undesirable in coal to be, used for making coke for iron industry, since it is transferred to the iron metal and badly affects the quality

and properties of steel. Moreover, oxides of sulphur (formed as combustion products) pollute the atmosphere and leads to corrosion.

#### Elemental composition of Coal

|  |  |
| --- | --- |
| **Carbon** | **60-96%** |
| **Hydrogen** | **2-6%** |
| **Nitrogen** | **1-2%** |
| **Sulphur** | **0.5-5%** |
| **Oxygen** | **1-30%** |

1. **Determination of Calorific Value (Heating Value)**

* Heating or Calorific Value is the amount of heat released when a unit mass of fuel is burned (Btu/lb. or cal/g)
* Calorific value has implications for pollution measurements such as SO2 whose emissions are calculated on a lb per million Btu basis

#### Fnits of heat :

1. **'Calorie'** is the amount of heat required to raise the temperature of one gram of water through one degree Centigrade (15-16°C).
2. "**Kilocalorie**" is equal to 1,000 calories. It may be defined as 'the quantity of heat required to raise the temperature of one kilogram of water through one degree Centigrade. Thus**: 1 kcal = 1,000 cal**
3. "**British Thermal unit" (B.T.F.)** is defined as "the quantity of heat required to raise the temperature of one pound of water through one degree Fahrenheit (60-61°F). This is the English system unit.

1 B.T.U. = 252 cal = 0.252 kcal 1 kcal = 3.968 B.T.U.

### Coal Ranks

* There are 4 general ranks for coals:
  + **Lignite** low rank

#### Sub bituminous

* + **Bituminous**
  + **Anthracite** High rank

#### CALORIFIC VALFE OF COAL FSING BOMB CALORIMETER

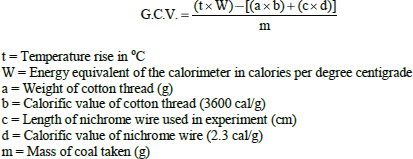
Weigh about 1 g of coal pellet and introduce it into the bomb.

1. Add 1 ml of distilled water and connect the fuse to the lid wires.
2. Pressurize the bomb with oxygen and place it inside the jacket.
3. Fill the jacket with 2000ml of water. Temperature of water must be 2oC less than the room temperature.
4. Assemble the calorimeter and run the motor for 5 minutes.
5. Record the temperature of the water bath accurately using a precision thermometer at an interval of 1 minute for 5 minutes and ignite the charge at the start of 6th minute

7) Keep recording the temperature every minute till constant temperature is attained.

1. Open the bomb carefully.
2. Wash all the interior surfaces of the bomb with the jet of distilled water and collect the washings in a beaker.
3. Remove all unburned pieces of the fuse wire and measure the length of the pieces.
4. Collect and weigh the residual ash

* Draw temperature versus time plot for the bomb calorimeter.
* Calculate the calorific value of coal from the data recorded.



# 13. Non Aqueous titrations

Organic compounds having definite acidic or basic properties may be determined by acid-base titrations. Titration in aqueous solution is limited in scope because many such compounds are sparingly soluble in water and also the acidic or basic strengths are so slight that a sharp end point cannot be obtained.

#### Why Non Aqueous??

* During the past four decades excess of newer complex organic medicinal compounds have taken cognizance in the therapeutic armamentarium. Evidently, these compounds posed *two vital problems of* quality control, both in pure and dosage forms by virtue of their inherent characteristics, namely :
* (*a) poor solubility in water, and*
* (*b) Weak reactivity in aqueous medium.*

#### In order to overcome these shortcomings the non-aqueous titrations were introduced.

* + Non-aqueous titrations have the following **advantages, namely :**
  + Elimination of poor solubility of substances.
  + Enhancement of weak reactivity of substances.
  + Selective titration by using suitable solvent and titrant of acidic/basic components of physiologically active moiety of a salt.
* Maintenance of speed, precision, accuracy and simplicity at similarity with classical methods of analysis, and
* Weak bases which have K*b values less than 10–6 can be titrated satisfactorily by non-aqueous* titrations.
* The reason being that in aqueous medium and at higher K*b values (> 10–6) the solvent* water competes progressively with the basic species in solution for the proton of the solvent.

#### TYPES OF SOLVENTS

The solvents for non-aqueous titrations are classified into 4 different types.

1. Aprotic solvents
2. Protophilic solvents
3. Prorogenic solvents
4. Amphiprotic solvents

#### Aprotic Solvents:

*Aprotic solvents are neutral substances, such as chloroform,* carbon tetrachloride and benzene, which are chemically rather inert. They neither gain nor lose electrons. They have a low dielectric constant, and do not react with either acids or bases. Ionisation is not likely to occur in such solvents. Aprotic solvents are often added to solvents which favour ionisation in order to depress solvolysis of the neutralisation product and so lead to a sharper end point.

#### Protophillic solvents:

**Phillic means liking. These solvents are basic in nature and can abstract proton from acids to give solvated protons.**

**HA + Sol. Sol.H+ + A-**

Acid + Basic Solvent Solvated Protron + Conj. base of acid

#### These solvents are classified into two types. They are strongly basic and weakly basic solvents.

A strongly basic solvent has stronger tendency to accept proton. These are called “Levelling solvents” because they can abstract proton from any acid, whether it is strong acid or weak acid. This effect is called “Levelling effect”.

Weakly basic solvents have weak tendency to accept proton. Hence these solvents are called as “Differentiating solvents”, because they can abstract proton from strongly acidic substances but not from weakly acidic.

#### Protogenic solvents:

Genic means producing. These are the acidic substances and produce protons when ionised. Solvents which are more acidic than water, include anhydrous acetic acid, anhydrous formic acid and concentrated sulphuric acid.

#### Amphiprotic Solvents:

These solvents have both protophilic and protogenic properties. i.e., being able to donate protons and accept protons.

* Ex: H2O, C2H5OH, CH3COOH H2O can accept proton as,

H2O + H+ H3O+ Which behaves as Base.

It can also donate proton and behaves as acid

H2O H+ + OH-

Similarly acetic acid being a weak acid, can show acidic property by dissociation into acetate ion and produce,

CH3COOH CH3COO- + H+

But in the presence of strong acid like perchloric acid, it can accept proton to form

“Onium ion”.

CH3COOH + HClO4 CH3COOH2+ + ClO4-

**Onium ion**

#### Solvents for NAT:

1. **Glacial Acetic Acid**

Glacial acetic acid is most frequently used non-aqueous solvent. Before it can be used, the water content in it should be adjusted between 0.1-1%. To adjust add sufficient acetic anhydride to convert any water into acetic acid.

#### Acetonitrile

Acetonitrile is frequently used with other solvents such as CCl4, Phenol & CH3COOH. It enables very sharp end points to be obtained in the titration of metal ethanoates.

#### Alcohols

Salts of organic acids esp soaps are best determined with mixture of glycols and alcohols. The most common combination is ethylene glycol and propan-2-ol

#### Dioxan

Dioxan is the another solvent which can replaces acetic acid

#### Dimethyl formamide

DMF is a protophillic solvent which is frequently employed in titrations between benzoic acid, amides etc...

#### Indicators

**S**

**No.**

**Indicator Preparation Colour change**

* 1. Crystal Violet 0.5% w/v in glacial acetic acid

Violet to blue followed by

green, finally greenish yellow

* 1. Methyl red 0.2% w/v in Dioxan Yellow-Red
  2. 1-Napthol benzene 0.2% w/v in acetic acid Yellow-green
  3. Quinaldine Red 0.1% w/v in ethanol Purple red-pale

green

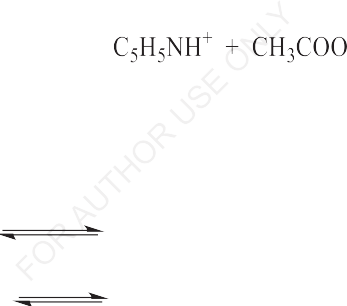
* 1. Thymol blue 0.2% w/v in methanol Yellow-blue
  2. Oracet blue B 0.5% w/v in acetic acid Blue-pink

#### NAT of weak bases using HClO4

**Principle**

Weak bases are dissolved in acetic acid and are titrated with acetous perchloric acid. Acetic acid behaves as weak acid because of poor dissociation of H+ ions, But when a strong acid like perchloric acid is added to acetic acid, there is a formation of onium ion which has more tendency to donate protons,

When weak base like pyridine is dissolved in acetic acid, equivalent amount of acetate ions are produced which have more tendency to accept protons,





Ultimately the titration of weakly basic compound in acetic acid against acetous perchloric acid yields accurate end point.





The net reaction is,

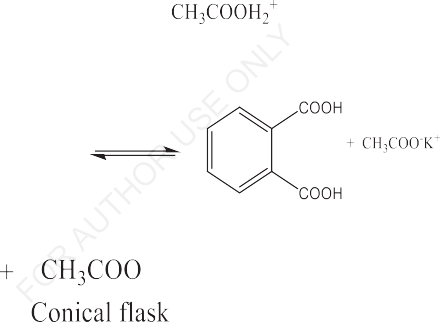
Hence the tendency of acid to donate proton is increased on the other hand, the tendency of the base to accept the proton is increased. This leads to the sharp end point in NAT.

#### Preparation of HClO4:

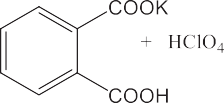
* 1. ml of HClO4 is taken into a beaker and add 500ml of acetic acid and 21ml of acetic anhydride. Cool the mixture and makeup to 1000ml with acetic acid. Water content adjusted between 0.02% to 0.05% using acetic anhydride.

#### Standardization:

Weigh out accurately 0.7g of potassium hydrogen phthalate and dissolve it in 50ml of glacial acetic acid. Add few drops of crystal violet indicator and titrate with perchloric acid solution until the violet colour changes to emerald green. Perform a blank titration using 50ml of glacial acetic acid and subtract the volume of HClO4 consumed.



* + - The net reaction is,



Each ml of 0.1N HClO4 = 0.02042g of KHP

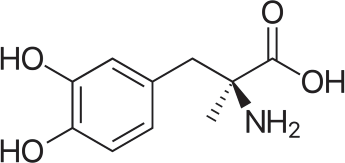
Strength of KHP = wt. Of KHP taken/vol.of HClO4 x 0.02042

#### Titration of primary, secondary and tertiary amines

* + - **Methlyldopa**

In general, the reaction taking place between a primary amine and perchloric acid may be expressed as follows :

R.NH2 + HClO4 ‹ [R.NH3]+ + ClO4-



**Materials Required** : Methyldopa 0.2 g ; anhydrous formic acid : 15 ml ; glacial acetic acid : 30 ml ; Dioxane : 30 ml ; 0.1 N perchloric acid and crystal violet solution.

**Procedure :** Weigh accurately about 0.2 g and dissolve in 15 ml of anhydrous formic acid, 30 ml of glacial acetic acid and 30 ml of dioxane. Add 0.1 ml of crystal violet solution and titrate with 0.1 N perchloric acid. Perform a blank determination and make any necessary correction.

#### Each ml of 0.1 N perchloric acid is equivalent to 0.02112 g of C10H13NO4. Some examples of drugs containing basic functional group:

**Name of Substance Qty. Prescribed Indicator**

**Employed**

Adrenaline 0.3 g Crystal Violet

**Calculations**

Each ml of 0.1 N HClO4 ÷ 0.01832 g of Cl9H13NO3

Levodopa 0.6 g Oracet Blue-B Each ml of 0.1 N

HClO4 ÷ 0.01972 g

of C9H11NO4

Metronidazole 0.45 g 1-Naphthol benzein

Nicotinamide 0.2 g Crystal Violet

Quinidine sulphate 0.4 g Crystal Violet

Each ml of 0.1 N HClO4 ÷ 0.01712 g of C6H9N3O3

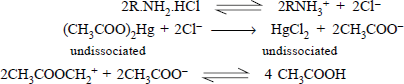
Each ml of 0.1 N HClO4 ÷ 0.01221 g of C6H6N2O

Each ml of 0.1 N HClO4 ÷ 0.02490 g

of (C20H24N2O2)2.H2SO4

#### Titration of Halogen Acid Salts of Bases

In general, the halide ions, namely : chloride, bromide and iodide are very weakly basic in character so much so that they cannot react quantitatively with acetous perchloric acid. In order to overcome this problem, mercuric acetate is usually added (it remains undissociated in acetic acid solution) to a halide salt thereby causing the replacement of halide ion by an equivalent amount of acetate ion, which serves as a strong base in acetic acid as shown below



#### ALKALIMETRY IN NON-AQFEOFS TITRATIONS

A excess of weakly acidic pharmaceutical substances may be titrated effectively by making use of a suitable non-aqueous solvent with a sharp end-point. The wide spectrum of such organic compounds include :anhydrides, acids, amino acids, acid halides, enols (viz., barbiturates), xanthines, sulphonamides, phenols, imides and lastly the organic salts of inorganic acids.

However, a weak inorganic acid e.g., boric acid, can be estimated conveniently employing ethylenediamine as the non-aqueous solvent.

#### Preparation of 0.1 N Potassium Methoxide in Toluene-Methanol

**Procedure :** Add into a dry flask, a mixture of methanol (40 ml) and dry toluene (50 ml) and cover it loosely. Carefully add freshly cut pieces of potassium metal to the above mixture gradually with constant shaking. After complete dissolution of potassium metal, add enough absolute methanol to yield a clear solution. Toluene 50 ml is added with constant shaking until the mixture turns hazy in appearance. The process is repeated by the alternate addition of methanol and benzene until 1 litre of solution is obtained, taking care to add a minimum volume of methanol to give a visible clear solution.

#### Standardization of 0.1 N Methoxide Solution

**Materials Required :** Dimethylformamide (DMF) : 10 ml **;** thymol blue (0.3% in MeOH) ; 0.1 N lithium methoxide in toluene methanol ; benzoic acid : 0.6 g.

**Procedure :** The apparatus shown in Figure 5.1, is employed for the standardization of 0.1 N methoxide solution. Transfer 10 ml of DMF in a conical flask and add to it 3 to 4 drops of thymol blue and first neutralize the acidic impurities present in DMF by titrating with 0.1 N lithium methoxide in toluene-methanol. Quickly introduce 0.06 g of benzoic acid and titrate immediately with methoxide in toluene methanol.

The various equations involved in the above operations are summarized as stated below :

##### Na + CH3OH ‹ CH3ONa + H2†

Interaction between sodium metal and methanol is an exothermic reaction and hence, special care must be taken while adding the metal into the dry solvent in small lots at intervals with adequate cooling so as to keep the reaction well under control.

#### *H2O + CH3*ONa ‹ CH3OH + NaOH H2CO3 + 2CH3ONa ‹ 2CH3OH + Na2CO3

iii) C6H5COOH + H—CON(CH3)2 HCON+H(CH3)2 + C6H5COO– (DMF)

CH3ONa CH3O– + Na+

HCON+H(CH3)2+ CH3O–‹ HCON(CH3)2 + CH3OH

#### Summing up :

**C6H5COOH + CH3ONa ‹ C6H5COONa + CH3OH**

**Step 1 : It shows the solution of benzoic acid (primary standard) in DMF, Step 2 : It depicts ionization of sodium methoxide,**

**Step 3 : It illustrates the interaction between the solvated proton and the methylated ion.**

**Some examples of drugs containing acidic functional group:**

**Name of**

**Substance**

**Qty. Prescribed**

**Indicator Employed**

**Calculations**

Allopurinol 0.2 g Thymol blue

Each ml of 0.1 N NaOCH ÷

3

0.01361 g of C H N O

5 4 4

Mercaptopurine 0.3 g Thymol blue

Each ml of 0.1 N NaOCH ÷

3

0.01522 g of C H N S

5 4 4

Amylobarbitone 0.5 g Quinaldine Red

Each ml of 0.1 N LiOCH ÷

3

0.02263 g of C H N O

11 18 2 3

Bendrofluazide 0.2 g Azo violet Each ml of 0.1 N NaOCH ÷

3

0.02107 g of C H F N O S

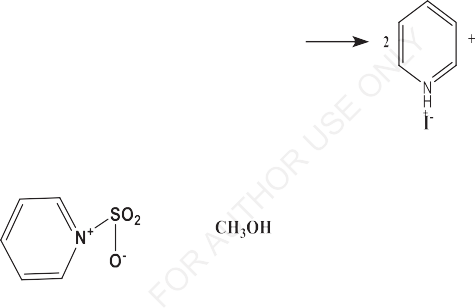
15 14 3 3 4 2

# 14. Determination of Moisture

**Karl Fischer Titration**

Chemical compounds such as organic solids, pharmaceutical substances etc.. may contain small amounts of water present in them. To determine the water present in such compounds, one of the most important method proposed by Karl Fischer (1935), which is considered to be relatively specific for water.

Karl Fischer proposed a reagent prepared by the action of sulphur di oxide upon iodine which is dissolved in pyridine and methanol. Water present in the analyte reacts with the Karl Fischer reagent in a two-stage process,



In order to stabilize the stoichiometry and shift the equilibrium further to the right, Fischer added pyridine (C5H5N) and used anhydrous methanol as the solvent. A large excess of pyridine was used to complex the I2 and SO2. In the first step, I2 and SO2 react in the presence of pyridine and water to form pyridinium sulfite and pyridinium iodide. Each one molecule of iodine disappears against each molecule of water present in the given sample. It is significant to mention here that in the presence of a large excess of pyridine (C5H5N), all reactants as well as the resulting products of reaction mostly exist as complexes as evident from above reactions. For volumetric analysis, the classical Karl Fischer reagent consists of I2, SO2, pyridine, and anhydrous methanol or another suitable solvent. The reagent decomposes on standing and must be standardized often.

#### Detecting the End Point:

An end point in a Karl Fischer titration can be observed visually based on the brown color of the excess reagent. The end-point of the Karl Fischer titration may be determined quite easily by adopting the electrometric technique employing the dead- stop end-point method. When a small e.m.f. is applied across two platinum electrodes immersed in the reaction mixture, a current shall tend to flow till free iodine exists. A situation will soon arise when practically all the traces of iodine have reacted completely thereby setting the current to almost zero or very close to zero or attain the end-point.

#### Applications:

Karl Fischer reagent has been applied to the determination of water in numerous types of samples. If the sample can be dissolved completely in methanol, a direct and rapid titration is usually feasible. This method has been applied to the determination of water in many organic acids, alcohols, esters, ethers, anhydrides, and halides. The hydrated salts of most organic acids, as well as the hydrates of a number of inorganic salts that are soluble in methanol, can also be determined by direct titration.

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