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Paper III Applied Analysis - I PRODIIVI

Unit - I : Analysis of ores:

Analysis is used to determine the composition of material. Analysis is a process of breaking a complex substance into smaller parts, which is to be analysed to gain a better understanding of it.

The field of chemistry uses analysis in atleast 3 ways.

a) To identify the components of a particular chemical composition.
b) To identify the proportions of components in mixture.
c) To breakdown chemical processes and examine chemical reactions between elements of matter.

Stages of Analysis:

A complete chemical analysis even for a single substance, involves a series of steps and procedures.

→ Sampling
→ Preparation of analytical sample
→ Dissolution of Sample.
→ Removal of Interferences
→ Sample Measurements
→ Result & Presentation of data.

Applied analysis regards the application of theories and principles of chemistry to practical purpose.

General techniques of Analysis Applied to Complex materials.

Chemical analysis is of particular importance in metallurgical industries b'cos the quality of finished prdts cannot be maintained without a knowledge of the correct composition of raw materials used as well as of finished products.

In metallurgical an industries, we perform the chemical analysis of raw materials, Prdts and by prdts.

There are 2 types of Analysis

① Qualitative analysis
② Quantitative analysis.

Qualitative analysis : This is the analysis deals with the identification of ions or elements present in the sample.

The Various tests performed for qualitative Assesment Includes – spot tests
– dry tests
→ solution tests.

Spot test : These are performed by placing one or two drops of the sample solution on a porcelian plate or absorbing paper and then reacting it with suitable reagents

Dry test : It includes the flame test for alkali metals, borax bead test and other tests where flame is used for fusion.

Solution test → It is the most commonly used. This is Performed in test tubes using Considerable Amounts of test solution and Reagents.

In all these cases (Spot / Dry / solution tests) the Specific colour is developed, precipitate formed and Similar other characteristics are the indications of specific substances present there.

Quantitative Analysis :

Quantitative analysis deals with the determination of how much of one or more Constituents present in the sample which may be solid, liq, gas or mixture.

Quantitative analysis is broadly divided into 2

① Classical methods
② Instrumental "

Classical methods :

The final measurement of substance is done by direct & indirect measurements of Volume and weight after proper tatment of a measured quantity of the material to be analysed.

These are classified into 2.

① Gravimetric analysis
② Volumetric "

Gravimetric Analysis :

The analysis is carried out by a Series of Weighing operations.

Volumetric Analysis / Titrimetric Analysis :

In this Analysis determines the volume of standard solution which is required to react quantitatively with a known volume of the other solution, the conc of which is to be determined.

→ 4 Cat These are classified into 4

(1) Acid-base titration
(2) Complexometric titration
(3) Redox titration
(4) Precipitation titration.

Advantages of classical mtds :

→ It gives the absolute data directly.
→ Do not require costly equipments
→ We can notice in earlier stage if anything goes wrong.
→ These are very suitable for the analysis of the major constituents as the % error is less.
→ Standard samples used for instrumental analysis are analysed only by classical methods.

Disadvantages

→ classical mtds do not provide informations about the physical and combined state of subs.
→ Quantity of sample req is large.
→ The process is very slow.
→ A small fraction of sample cannot be analysed.

Instrumental method:

Instrumental methods of analysis are usually much faster than classical mtds.

* In instrumental methods any physical measurements may (Absorption, Emission, Scattering, Potential, Conductivity etc) are used to give the desired analytical result.
* Comparison of samples are done using standard samples of known analysis to know the physical property (ie either absorption, emission etc).

Advantages:

→ It provides more information than classical mtds
→ We can estimate the components which are in little amounts.
→ A small fractions can be analysed
→ Speed of analysis is more.

Disadvantages:

→ Instrumental mtd do not give absolute data. A calibration with standard sample is required.
→ Regular checking of apparatus and whole equipments by means of standard sample is required.
→ Results obtained are less accurate than classical mtds.
→ The cost is quite high.
→ Due to complicated nature of instruments, they are often subject to interferences.

Scope of Metallurgical Analysis

Metallurgical analysis basically involves the qualitative as well as quantitative analysis of various raw materials, metals, alloys, by products and other materials.

* Qualitative analysis deals with the identification and separation of substance and the chemical principles involved in the procedures.

→ The Qualitative analysis in metallurgical fields is particularly essential prior to Quantitative analysis of unknown substance

* Quantitative analysis is concerned with the determination of the amount of an element or chemical substance present either alone or in a mixture of other substances.

Metallurgical analysis usually consists of four major steps:

1. Sampling, that is selection of representative sample of the material to be analysed.
2. Conversion of the desired constituents into a form suitable for measurement
3. Measurement
4. Calculation and interpretation of the measurement.

General methods for dissolution of Complex materials.

The methods used for dissolution of Complex materials are ① Standard solution mild
② Standard fusion process.

Standard solution process:

Naturally occurring minerals and ores, various alloys etc., are usually treated with different reagents in order to bring them in solution form.

Acids and Acid Mixtures are normally commonly used for the dissolution of these materials. These are added according to the nature of the constituents present.

Strong mineral acids are good solvents for many inorganic solids.

HCl → is good general solvent for dissolving metals which are above hydrogen in electromotive series.

HNO_3 → is strong oxidising agent and dissolves most of the common metals, non-ferrous alloys and the acid insoluble sulphides.

$HClO_4$ → $HClO_4$, when heated to drive off water, becomes a very strong and efficient oxidising acid in the dehydrated state.
It dissolves most of the common metals & destroys organic matter)
It must be used in extreme caution, because it will react explosively with many easily oxidisable subs specially organic matter.

H_2SO_4 → Many materials are decomposed and dissolved by hot conc. H_2SO_4.
As boiling point of H_2SO_4 is very high (about 340°C)

Most of the Organic comp are dehydrated and oxidised at this temp and thus eliminated from the sample as CO_2 and H_2O by this wet ashing process

HF - (HF is used for the decomposition of silicate rocks and minerals in the analysis of elements other than silica.)
HF is used with other acids in dissolving steel, which is difficult to dissolve in other solvents.

To decompose samples, some oxidising agents are used as the mixture of acids. Such as

① Aquaregia → 3:1 of HCl : HNO_3.
② The addition of Br_2 or H_2O_2 to mineral acids generally increases their solvent action.
③ Mixtures of HNO_3 and $HClO_4$ are also used for this purpose and are less dangerous than perchloric acid alone.

→ For Siliceous Ores → HCl is commonly used.
For Sulphide Ores → conc. HNO_3 is used.

Standard Fusion process :

Substance which are insoluble or only partially soluble in acids are brought into solution by fusion.

The fusion reagents are generally called fluxes.

Flux is an alkali metal salt, used to decompose the substance which are attacked by the reagent very slowly.

The flux employed will depends on the nature of the insoluble substances.

Usually for 1 part by weight of ore 10 parts by weight of the mixture are used.

Metallic Crucibles, preferably of platinum, is employed for carrying out the fusion.

Procedure:

→ 3 parts Na_2CO_3 & 2 parts K_2CO_3 mixture

A layer of fusion mixture is placed at the bottom of the crucible and then an intimate mixture of the flux and the finely ground subs is added.

The crucible is first heated gradually till all the moisture and greater part of CO_2 have been expelled and then at red hot until the mass is completely fused. The crucible is grasped by means of a tong and gently rotated so that the molten material distributes itself around the walls of the container and solidifies there in a thin layer. This procedure The crucible is cooled, placed in water and warmed till the mass is completely dissolved. Then Acid is added to acheive solution.

Most commonly used fluxes are anhydrous Sodium and potassium Carbonates. These are used alone or less frequently, mixed with other fluxes like Potassium nitrate, Sod. peroxide, Sod | Potassium pyrosulphates & Sod | Potassium hydroxides.

Types of fluxes.

Basic fluxes

Acidic fluxes

Oxidising "

Red

Basic fluxes → These are alkali metal carbonates, hydroxides, peroxides, and borates.

→ These basic fluxes are used to attack acidic materials.

Acidic fluxes → These are pyrosulphates, acid fluorides, boric oxide.

Oxidising fluxes → Sodium peroxide.

Common fluxes.

Flux	Melting pt °C	Type of crucible used	Type of subs Decomposed
Na_2CO_3	851	Pt crucible	Silicates. Silica Containg Samples, Alumina containg Samples, Sparingly Soluble phosphates & Sulphates.
Na_2O_2 (Oxidising flux)		Fe, Ni Crucibles	for sulphides, acid insoluble alloys of Fe, Ni, Cr, Mo, W, Li. Pt alloys, Cr, Sn, Zr minerals.
$K_2S_2O_7$ (Acid flux)	300	Pt, Porcelain Crucibles	for slightly soluble Oxides and oxide containing Samples

Analysis of iron ore:

Determination of Moisture Content:

1) For determination of moisture content, Take a cleaned pt/porcelin crucible and heat it for about 20 minutes
→ Cool in a dessicator and weigh.
→ Again heat the crucible, cool and weigh.
→ Repeat the process until constant weight is obtained which is denoted as (W_1).
2) Take 5-10 g. of sample into the crucible which is preweighed.
3) Heat the crucible for 1 hr at 105-110°C
4) Cool the crucible with sample, and then weigh. Repeat the process until constant weight is obtained which is (W_2).
5) The difference in the weights ($W_2 - W_1$) gives the amount of moisture content present in the sample.

$$\% \text{ Moisture content} = \frac{W_2 - W_1}{\text{wt of sample}} \times 100$$

Determination of loss on ignition:

1) Take 1g of sample in a platinum or porcelain crucible. Weigh the sample along with crucible and noted as W_1
2) Ignite first for about 450-500°C for 5 minutes
3) until the crucible becomes red hot.
3) And then again undergo ignition at the temperature of 900-1100°C for 30 minutes
4) And Weigh the sample until constant reading

is obtained, and noted as W_2.

(5) The difference in the weight (loss in weight) gives the loss on ignition

$$\% \text{ loss on ignition} = \frac{W_1 - W_2}{\text{Wt of Sample}} \times 100$$

Determination of Total Iron :

Total iron present in the iron ore sample can be determined using Volumetric analysis by Potassium dichromate method.

Principle :

The ore which is present in oxides form is dissolved in Hcl solution.

The ore which is present in sulphides forms is dissolved by aquaregia.

Both are evaporated to fumes with H_2SO_4 and redissolved in conc. Hcl.

$FeCl_3$ ~~~ Fe

$$2FeCl_3 + SnCl_2 \rightleftharpoons 2FeCl_2 + SnCl_4$$

(III) (reducing agent) (II)

$$SnCl_2 + 2HgCl_2 \rightleftharpoons SnCl_4 + Hg_2Cl_2$$

$$6FeCl_2 + K_2Cr_2O_7 + 14HCl \rightleftharpoons 6FeCl_3 + 2KCl + CrCl_3 + 7H_2O$$

Reagents Required

(1) Std $K_2Cr_2O_7$
(2) $SnCl_2$ (Stannous chloride)
(3) $HgCl_2$ (mercuric chloride)
(4) DPA indicator. (Diphenyl Amine).

Procedure :

(1) Take 0.5 - 1g. of finely ground iron ore sample in 250 ml conical flask.
(2) To this add 10 ml of HCl for dissolution
(3) Warm gently for 10-15 min and then increase the temperature until it boils.
(4) And then evaporate it to dryness.
(5) The mass is dissolved in some HCl & boiling
(6) Heat the solution to boiling and, add to it Stannous chloride ($SnCl_2$) drop by drop. with continous shaking until all the red colour of $FeCl_3$ is completely discharged.
(where $FeCl_3$ (III) + $SnCl_2$ → $FeCl_2$ (II) + $SnCl_4$)
(7) A slight excess of $SnCl_2$ solution is added to complete reduction of Fe(III) → Fe(II).
(8) Quick cooling is done after adding $SnCl_2$ because to prevent re oxidation of reduced soln by atmospheric oxygen.
(9) Add 10 ml of $HgCl_2$ solution to the above solution and dilute it to 200 ml using distilled water.
($HgCl_2$ addition is made to take care of the excess $SnCl_2$.)

(10) $HgCl_2$ solution is done in cold reduced solution. (In hot condition $HgCl_2 + SnCl_2 \rightleftharpoons Hg + SnCl_4$ may takes place, precipitating mercury in a very finely divided state). So this mercury will oxidised by $K_2Cr_2O_7$ and shows high % of iron).

(11) Then the above solution is titrated with standard Potassium dichromate solution ($K_2Cr_2O_7$) using DPA as indicator.

(12) The end point will be colourless to Pale blue colour when the oxidation of Fe(II) to Fe(III) is completed.

(13) The sharpness of indicator as end point can be improved by adding conc H_2SO_4 and Dil H_3PO_4 and water.

% of total iron can be known by the how much volume consumed by $K_2Cr_2O_7$.

$$\% \text{ Total Iron} = \frac{\text{Vol of } K_2Cr_2O_7 \times \text{Conc of } K_2Cr_2O_7 \times C}{\text{Weight of the sample}} \times 100$$

$C = \frac{\text{1ml of } 0.05/0.1N\ K_2Cr_2O_7}{} = x\ g$ of total iron

Determination of Fe(II)

Method: Fe(II) can be determined using Volumetric method.

Reagents req:

(1) Sodium bicarbonate ($NaHCO_3$).
(2) Hcl, HF, H_3PO_4
(3) Barium Diphenyl amine Sulphonate
(4) Potassium dichromate ($K_2Cr_2O_7$).

Procedure:

(1) Take 0.5 g of ore sample in 500 ml conical flask which is fitted with bunsen value.
(2) Dilute the sample with water and add 1g of $NaHCO_3$, 50 ml of Hcl, 4 drops of HF.
(3) The contents are digested for 5-10 min with bunsen value in position
(4) Wash carefully and remove the value and dilute the content of flask with 250 ml cold distilled water.
(5) Add 10ml of H_3PO_4 and Barium DPA sulphonate indicator and titrated against $K_2Cr_2O_7$ sol^n
(6) The end point is colour change to purple colour.
(7) The volume consumed by $K_2Cr_2O_7$ represents the percentage of iron present in sample.

$$\% Fe(II) = \frac{\text{Vol of } K_2Cr_2O_7 \times \text{Conc of } K_2Cr_2O_7 \times C \times 100}{\text{wt of Sample}}$$

C = 1.0ml of 0.05N $K_2Cr_2O_7$ = x g of fe (II).

Determination of Fe(II) by photochemical reduction mtd.

Determination of Silica (SiO_2):

Silicates are divided into two classes

a) soluble silicates
b) Insoluble silicates

Soluble silicates → decomposed by acids such as Hcl, to form silicic acid. &

Insoluble silicates → which are not decomposed by acids.

Determination of Silica in an Insoluble silicate

Method → Gravimetric analysis.

Principle → Insoluble silicates are generally fused with sodium carbonate and forms melt, which forms sodium silicate i.e, dissolved in Hcl and forms $SiO_2 \cdot xH_2O$ (silicic acid). The residue is heated, dried and undergo ignition. To obtain more accurate results, hydrofluorination is done for determination of silica.

$$SiO_2 + Na_2CO_3 \rightarrow Na_2SiO_3.$$

$$Na_2SiO_3 + HCl \longrightarrow SiO_2 xH_2O$$
(silicic acid).

$$SiO_2 xH_2O \xrightarrow{\text{dried}} SiO_2.$$

$$SiO_2 + HF \xrightarrow{H_2SO_4} H_2[SiF_6]$$

$$H_2[SiF_6] = SiF_4 \uparrow + 2HF.$$

The evolved SiF_4 gives the amount of SiO_2 present in the sample.

Reagents

→ Hcl
→ Fusion mixture

Procedure:
1) Take 1g of
Crucible.
2) To that
and
3)

Procedure :

1) Take 1g of sample accurately in Pt / Porcelain Crucible
2) To that add 6 times of fusion mixture (Na_2CO_3, K_2CO_3) And undergo fusion.
3) Heat the mixture for 20 minutes and Again add fusion mixture and undergo Ignition by covering the lid.
4) A Semi Solid melt is formed. which is allowed to cool.
5) This melt is slowly dissolved by adding Conc. HCl solution.
6) Evaporate the contents to complete dryness
7) Heat the residue for an hour; at 100-110°C to dehydrate the silica.
8) Moisten the residue with 5 ml conc HCl Again add distilled water. Rinse. Filter the Separated silica on a whatmann No 41 filter Paper which is taken in preweighed crucible (W_1)
9) Wash the precipitate with dil HCl and then with hot water (until free of chlorides)
10) Moisten the residue (precipitate) with 15
11) for determination of exact SiO_2 content. to the residue add 1 ml water, a 2-3 drops of H_2SO_4 and 5 ml of HF (pure).
12) Evaporate to dryness & Ignite again.
13) Silica volatilises as SiF_4.
14) Weigh again. (W_2)
15) The loss in weight ($W_2 - W_1$) gives the amt amount of silica.

$$\% Si = \frac{W_2 - W_1 \times C}{\text{Weight of sample}} \times 100$$

$$C = Si / SiO_2$$

Determination of Soluble Silicate

Method: Gravimetric method.

Principle:

$$\underset{(Si)}{\overset{FeSi}{\text{Sample}}} + HCl + H_2O \longrightarrow SiO_2 \cdot xH_2O$$

$$SiO_2 \cdot xH_2O + \xrightarrow{\Delta} SiO_2$$

$$SiO_2 + 6HF \longrightarrow H_2[SiF_6] + 2H_2O$$

$$H_2[SiF_6] \longrightarrow SiF_4 \uparrow + 2HF.$$

Reagents: HCl., H_2SO_4, HF.

Procedure:

1. Take 1g of sample (iron ore) in a cleaned Pt / Porcelain crucible.
2. To this sample add distilled water and stir well. And then add 25 ml of 1:1 HCl stir well and heat the solution until it evaporate to dryness.
3. Stir the residue well and is dried at 105–110°C. under Oven. to dehydrate silica.
4. Again Moisten the residue with distilled water and HCl.
5. Filter off the solution using whatmann No-1 filter paper. Filtrate is preserved.
6. The precipitate obtained is washed with hot water and dil HCl (until, ppt free of all chlorides) and ppt is taken in preweighed crucible (W_1).

(7) The precipitate is moisten with water and add 2 or 3 drops of H_2SO_4 and 5ml HF.
(8) Heat the solution until HF is evaporated as $SiF_4\uparrow$, dried and ignited.
(9) Allow to cool in dessicator and weigh and noted as W_2.

The loss in weight gives the amount of silica evaporation

$$\%Si = \frac{W_2 - W_1 \times C}{W_1 \text{ of sample}} \times 100$$

$$C = Si/SiO_2$$

Note:
H_2SO_4 is added before HF in hydrofluorination necessary, else other oxides will also be converted to fluorides and will be volatise

~~Determination of Alumina (Al_2O_3)~~:

The filtrate obtained from silica (SiO_2) is used to determine Al_2O_3, TiO_2, MgO, Ca

→ filtrate is oxidised with 1-2 ml HNO_3 and boiled to reduce the bulk.
→ Cool the solution and add 2ml of bromin
→ Add 5-10 g NH_4Cl and sufficient amount of NH_3 to make it ammonical solution.
→ Boil 2-3 minutes to expel $NH_3\uparrow$
→ Filter the solution
→ Filtrate is collected separately.
→ Precipitate obtained is dissolved in Hcl a

Repeat the R_2O_3 and NH_4OH separation and again filter.

Filtrate is two which is collected is preserved for determination of CaO & MgO.

The precipitate is used for determination of Al_2O_3 and TiO_2.

Determination of Al_2O_3:

Method: Alumina (Al_2O_3) can be determined using Gravimetric method.

Principle:

$$AlCl_3 + NH_4OH + Na_3PO_4 \longrightarrow AlPO_4 \downarrow$$

$$AlPO_4 \xrightarrow[\text{ignition}]{\Delta} Al_2O_3.$$

Reagents: NH_4OH, sodium phosphate, sodium-thio crystals, acetic acid, ammonium-acetate.

Procedure:

1. Collect the precipitate which is obtained from silica filtrate.
2. That is dissolved in HCl. To this solution add 15 ml of cold saturated solution of Sodium phosphate and ammonium hydroxide till a faint ppt is formed.
3. Dissolve the ppt with excess of HCl.
4. Add 12 ml of Glacial acetic acid and 10g of Sodium thio crystals. (these are added to keep iron in the solution in ferrous state)

(5) Dilute and
(6) Add 5ml
(7) Filter the

(5) Dilute with distilled water and boil.
(6) Add 5ml of ammonium acetate and again boil
(7) Filter the solution. (PPt obtained is $AlPO_4$)
(8) Precipitate obtained is taken in pt / silica crucible which is preweighed. (W_1)
(9) Ignite gently at first & strongly to about 900°-1100°C
(10) Cool under dessicator
(11) And weigh the sample (W_2).

$$\% Al = \frac{W_2 - W_1 \times C}{\text{wt of Sample}} \times 100$$

$C = Al/Al_2O_3 = Al/AlPO_4$.

Determination of Titania (TiO_2):

Method: Colorimetric method
(Visual colour comparison method).

Principle: The unknown sample which is to be determined is compared with std sample of TiO_2.

With acidic titanium solution, hydrogen Peroxide produces a yellow colour with small amounts of titanium.

The Intensity of colour is proportional to the amt of element present.

And comparison is made with std titanium solution.

Reagents: H_2O_2, H_2SO_4, $KHSO_4$ (Potassium bisulphate), Std solution of TiO_2

Std solution of TiO_2 (Preparation):

0.75g of Potassium fluotitanate (K_2TiF_6) is weighed and add 2-3 ml of H_2SO_4 to it. The mixture is evaporated to dryness until strong fumes. This procedure is repeated 3 times to expel all fluorine. The mass is dissolved in 5% H_2SO_4 solution and diluted to 250 ml.

Procedure:

(1) If TiO_2 (titania) which is present in the ore will be precipitated along with $AlPO_4$.
(2) Collect the $AlPO_4$ precipitate from after ignition.
(3) To that add 2-3g fusion mixture in a pt crucible. Melt is formed. ie, dissolved in distilled water.
(4) Al_2O_3 remains in solution, TiO_2 is precipitated
(5) Filter the solution. The precipitate is washed with hot water and undergo ignition.
(6) Cool and add 1g of $KHSO_4$ (pot. bisulphate) in crucible and fuse for 2-3 min.
(7) Cool the melt & add H_2SO_4 and filter.
(8) To that add 2ml of H_2O_2 solution, yellow colour is obtained.

This yellow Coloured Solution is Compared using Standard solution of TiO_2.

from molⁿ formula

240.3 g K_2TiF_6 ⟶ 80.09 g of TiO_2

0.75 g K_2TiF_6 ⟶ x

$$x = \frac{80.09 \times 0.75}{240.3} = 0.25\ g\ TiO_2$$

0.25 g TiO_2 is dissolved in 250 ml distilled water.

∴ 1ml of std solution = 0.001 g of TiO_2.

By this we can determine the amount of TiO_2 present in sample.

Determination of lime (CaO):

Method: The method used is Gravimetric method

Principle: Calcium is precipitated as calcium oxalate $CaC_2O_4 \cdot H_2O$ by treating a hot HCl sol with ammonium oxalate and slowly neutralising with aqueous NH_3 solution.

$$Ca^{2+} + C_2O_4^{2-} + H_2O \longrightarrow CaC_2O_4 \cdot H_2O$$

$$Ca^{2+} + (NH_4COO)_2 \longrightarrow \underset{(Calciumoxalate)}{Ca(COO)_2}\downarrow$$

$$CaC_2O_4 \xrightarrow{\Delta} CaCO_3 + CO$$

$$CaCO_3 \xrightarrow[1200°C]{\text{Ignition}} CaO + CO_2$$

Procedure

(1) Collect the filtrate from silica (SiO_2) so that filtrate solution add 10ml of water and followed by addition of HCl.
(2) Heat the mixture and boil gently for several minutes to expel CO_2.
(3) Rinse well and it is diluted to 200ml with water.
(4) Heat the solution to boiling, add a warm solution of 20g of ammonium oxalate in 50 ml of water.
(5) To that resultant solution 1:1 dilute ammonia solution is added dropwise until the mixture is neutral or faintly alkaline.
(6) Allow the solution to stand for 1 hr.
(7) After precipitate is settled, filter the solution
(8) The precipitate is again washed with dil few drops of ammonium oxalate solution.
(9) The precipitate Calcium oxalate ($CaC_2O_4 \downarrow$) which is formed is taken in pt crucible which is Preweighed (W_1).
(10) Precipitate is dried under oven for 100 - 120°C for 1hr
(11) And undergo ignition at the temp of 1100°C.
(12) Cool the crucible under dissicator and again weigh which is noted as (W_2).
(13) The difference in the weights gives the amount of precipitate obtained.

$$\% CaO = \frac{W_2 - W_1 \times C}{\text{Wt of Sample}} \times 100$$

$$C = CaO / CaC_2O_4$$

* Note (Precaution)

As CaO absorbs CO_2 from atmosphere, precaution should be taken while weighing. This can be prevented by keeping small amt of Sod. lime in balance

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Determination of lime (volumetric analysis)

Mtd → Volumetric analysis.

Principle →

$Ca^{2+} + (NH_4)_2C_2O_4 \longrightarrow CaC_2O_4 \downarrow$

$CaC_2O_4 + H_2SO_4 \longrightarrow CaSO_4$ (white) $+ H_2C_2O_4$

$5H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 \xrightarrow{\text{dil } H_2SO_4} K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$

Reagents → Amm. oxalate, H_2SO_4, $KMnO_4$

Procedure →

① Bo collect the filtrate from SiO_2. This filtrate is boiled.

② To this solution add 30 ml of saturated boiling hot solution of ammonium oxalate.

③ Continue boiling for 3-4 minutes longer.

④ Allow the precipitate to settle for about 1hr.

⑤ Filter off the precipitate and wash it until it is free of ammonium oxalate with hot water.

⑥ Reserve the filtrate & washings for the determination of MgO.

Test for absence of ammonium oxalate: take washings in a test tube. It is acidify with few drops of 6N H_2SO_4. Boil and add 1 or 2 drops of std $KMnO_4$. If pink colour persists, the precipitate is free of from Ammonium Oxalate).

⑦ When it is free of ammonium oxalate, filter the solution

⑧ The precipitate is collected and is washed with hot water and 15 ml of H_2SO_4 solution and wash again with hot water.

⑨ The precipitate is dissolved due to presence of H_2SO_4.

(10) Heat the calcium oxalate solution to about 70°C. and titrated with $KMnO_4$ solution.

(11) The volume consumed by $KMnO_4$ gives the amount of CaO obtained.

$$\% CaO = \frac{\text{Vol of } KMnO_4 \text{ consumed} \times \text{Conc of } KMnO_4 \times C}{\text{Wt of Sample}} \times 100$$

C = 1ml of 0.05N $KMnO_4$ = x g of CaO.

Determination of MgO (Magnesia):

Method: It can be determined using both Graumetric and volumetric methods using ammonium phosphate.

Gravimetric method:

Principle:

$$MgCl_2 + (NH_4)_2HPO_4 + NH_4OH \longrightarrow MgNH_4PO_4 \downarrow + 2NH_4Cl + H_2O$$

$$MgNH_4PO_4 \xrightarrow{\text{Ignition}} Mg_2P_2O_7$$
(Mag. pyrophosphate)

Reagents:

Ammonium phosphate $(NH_4)_2HPO_4$,
Ammonium hydroxide
Ammonia solution.

Procedure:

(1) Collect filterate from Silica & filtrate frm CaO
(2) To that add 3ml of conc HCl and evaporate to reduce the volume to half
(3) Add 20 ml of Saturated solution of ammonium phosphate $(NH_4)_2HPO_4$ to the hot boiling solution
(4) Stir well. And add 100 ml of Ammonia (NH_3) solution.

(5) The precipitate is observed which is Magnesium Ammonium phosphate ($MgNH_4PO_4$)
(6) Allow the precipitate to settle for 2 hours and filter.
(7) The precipitate is washed with ammonia solution.
(8) The precipitate is transfered wit into the Pt/porcelain crucible. (W_1)
(9) It is dried under oven at 105-110°C
(10) And undergo ignition at the temperature of 900-1100°C.
(11) The ppt is decomposed to magnesium pyro phosphate ($Mg_2P_2O_7$)
(12) It is cooled and weighed (W_2).
(13) The difference in weights ($W_2 - W_1$) gives the amt of MgO.

$$\% MgO = \frac{W_2 - W_1 \times C}{\text{wt of sample}} \times 100$$

$C = MgO / Mg_2P_2O_7$.

Volumetric method:- (Det of MgO) (Magnesia)

Principle: $MgCl_2 + (NH_4)_2HPO_4 + NH_4OH \rightleftharpoons MgNH_4PO_4 + 2NH_4Cl + H_2O$.

Reagents:
Ammonium phosphate, Ammonium hydroxide, Ammonia, acid H_2SO_4, NaOH.

Procedure :

(1) Collect the filtrate from SiO_2 and CaO.
(2) To that add 3ml of conc HCl and evaporate to dryness until the volume reduced to half
(3) To this add 20ml of saturated solution of ammonium phosphate $(NH_4)_2HPO_4$. Stir well
(4) Add ammonia solution with stirring.
(5) Allow the precipitate to settle. which is Magnesium ammonium phosphate ($MgNH_4PO_4$).
(6) The precipitate is washed with ammonia solution
(7) ~~Add this precipitate is transfered into porcelain crucible~~
(8) The precipitate is dried under oven at 50-60°C for 15 minutes
(9) Place the residue and filter paper in beaker.
(10) Add excess of H_2SO_4 solution from burette until the residue is dissolved.
(11) Dilute the solution with distilled water.
(12) Titrated back the solution with NaOH solution.
(13) The volume consumed by H_2SO_4 gives the measures amount of MgO present in the sample.

$$\% MgO = \frac{\text{Volume consumed by } H_2SO_4 \times \text{Conc of } H_2SO_4 \times C}{\text{wt of sample}} \times 100$$

C = 1ml of 0.05N H_2SO_4 = x g of % MgO sample.

Determination of Total Sulphur:

Method: Gravimetric method.

In Iron ore, sulphur exists in the form of Pyrite and Manganese sulphide.

$$S^{2-} + HNO_3 \longrightarrow SO_4^{2-}$$

$$SO_4^{2-} + BaCl_2 \longrightarrow BaSO_4 \downarrow$$

Note: $SO_4^{2-} + Na_2CO_3 \longrightarrow Na_2SO_4$ | $Na_2SO_4 + BaCl_2 \longrightarrow BaSO_4$

Na_2CO_3 is used to fix SO_4^{2-} as Na_2SO_4 where it at high temp it doesn't undergo decomposition

Reagents: HNO_3, HCl, Na_2CO_3 (fusion mix), ammonia, $BaCl_2$ solution

Procedure:

1. Take 1g of iron ore sample ore in a cleaned beaker.
2. To this add 40ml conc HNO_3 and 5 ml of conc HCl and heat it for 1 hr.
3. Transfer the solution into porcelain dish add a pinch of Na_2CO_3 and heat it until it evaporates to dryness.
   [Na_2CO_3 is added to fix sulphate formed due to oxidn of sulphides by aquaregia in the form of Na_2SO_4.
4. Ignite at red hot to destroy organic matter and to dehydrate H_2SiO_4.
5. Cool the ignited residue and add 25 ml conc. HCl until it dissolve.
6. Dilute to about 50 ml with water and filter off SiO_2.
7. Wash with 10% HCl. To the filtrate add excess of Ammonia solution.
8. Keep the liq at 70°C for abt 15 min
9. Cool & dilute.

(10) Neutralise the filtrate with Hcl by adding 2-3 drops of methyl orange and 1ml conc Hcl in excess

(11) Heat the solution until it boils and add boiling hot solution of $BaCl_2$ so

(12) Stir vigorously and allow to stand for about 30 minutes for ppt to settle

(13) Filter the solution and ppt is washed until it is free from chloride and taken in crucible (W_1)

(14) The precipitate is dried under oven at 105-110°C and undergo Ignition

(15) Cool it under desicator and weigh as $BaSO_4$. (W_2)

$$\% S = \frac{W_2 - W_1 \times G}{\text{Wt of Sample}} \times 100 \quad ; \quad G = S/BaSO_4$$

Determination of P_2O_5 (Det of P as P_2O_5)

Method → Volumetric method.

Principle → The sample is heated with ammonium molybdate in presence of HNO_3 acid forms ammonium phosphomolybdate which is titrated with H_2SO_4 in presence of excess NaOH.

Reagents →

Na_2CO_3, HNO_3, $KMnO_4$, $NaHSO_3$, NaOH, Phenolphthalein Indicator.

Procedure →

(1) Collect 1g of sample (iron ore) and dissolved in 40ml conc Hcl in a beaker

(2) Heat the solution until it evaporates to dryness.

(3) Again add 20ml conc. Hcl until it dissolve and dilute it with water. Filter.

(4) Ignite the residue and wash and filtrate (1) is preserved.

(5) To the residue add fusion mix and fused.
(6) i.e, the mass is diluted with distilled water and filter again. Filtrate (2) is collected

(7) Combine ① & ② filtrates add 30 ml conc HNO_3 and evaporate to half and again add HNO_3

(8) Heat the solution to boiling and add solution of $KMnO_4$ until pink colour persists.

(9) Continue heating and destroy excess $KMnO_4$ with Na_2SO_3. Cool the soln

(10) Add ammonium Molybdate soln. shake

(11) Precipitate is formed Ammonium phospho-Molybdate. Filter. Wash ppt several times with HNO_3.

(12) To the precipitate is dissolved in a known/measured quantity of std NaOH solution from burette and shake.

(13) And titrate the excess NaOH with HNO_3 solution using phenolphthalein indicator.

(14) The volume consumed by NaOH will give the measure of amount of phosphorous content in the ore.

$$\% P = \frac{\text{Vol of NaOH} \times \text{Conc of NaOH} \times G}{\text{wt of Sample}} \times 100$$

c = 1ml of 0.05N NaOH = x g of Phospholaus

RXN

$Fe_3P + HNO_3 \longrightarrow 3Fe(NO_3)_2 + PH_3 + 4H_2O + 2NO$

$3PH_3 + 8HNO_3 \longrightarrow 3H_3PO_4$ (Orthophosphoric) $+ 4H_2O + 8NO$

$3PH_3 + 8HNO_3 \longrightarrow 3H_3PO_3$ (m. Phosp. acid) $+ 4H_2O + 8NO$

$H_3PO_4 + 21HNO_3 + 12(NH_4)_2MoO_4 \longrightarrow (NH_4)_3PO_4 \cdot MoO_3 + NH_4NO_3 + 12H_2O$

$(NH_4)_3PO_4 \cdot MoO_3 + 26NaOH \longrightarrow (NH_4)_2HPO_4 + 12(NH_4)_2MoO_4 + Na_2MoO_4 + H_2O$

Gravimetric Mtd (Phosphorous)

Reaction

$HPO_4^{2-} + (NH_4)_2MoO_4 + H^+ \longrightarrow$

$\therefore (NH_4)_3[PMo_3O_{10}(OH)_4] + 12H_2O$

(Amm. phosphomolybdate)

yellow ppt.

Reagents → Amm. Molybdate

HNO_3 (for start) / HCl

Procedure:

(1) Take 1-2 g of iron ore sample. It is dissolved in 40ml Conc HCl in beaker

(2) Heat the solution until it evaporates to dryness

(3) Again redissolve using conc HCl solution filter

(4) To the filtrate add HNO_3 solution

(5) And then heat it until it boils

(6) Now add Ammonium Molybdate solution and warmed to 60°C. Stir well.

(7) Allow the precipitate to settle. And then filter

(8) The precipitate (Amm. phospho Molybdate) ppt obtained is taken in pre-weighed crucible (w_1) and wash ppt with HNO_3 (or) Amm. nitrate sol^n.

(9) Dry the ppt at 105-110°C and then undergo ignition at 900-1100°C. Cool it under desiccator.

(10) And weigh the sample (w_2) as $P_2O_5 \cdot 24MoO_3$

(11) The difference in weights gives the amount of phosphorous.

$$\% P = \frac{w_2 - w_1 \times C}{\text{wt of sample}} \times 100$$

, $C = P / P_2O_5 \cdot 24MoO_3$

$C = P / (NH_4)_3(PMo_3O_{10})_4$

Determination of Manganese:

Method: Gravimetric method.

Reaction:

$$(NH_4)_2HPO_4 + MnCl_2 \longrightarrow \underset{\text{Manganese Ammn phosphate}}{MnNH_4PO_4}$$

$$MnNH_4PO_4 \xrightarrow{\Delta} \underset{\text{Manganese Pyrophosphate}}{Mn_2P_2O_7}$$

Reagents:

di Amm. Hydrogen phosphate, HCl, NH_3 soln
Amm. chloride.

Procedure

1. Take 1-2g of iron ore sample and it is dissolved in dil. HCl solution
2. The solution is neutralised with dil NH_3 and 20g NH_4Cl and excess of diammonium hydrogen phosphate, $(NH_4)_2HPO_4$.
3. Heat the solution to boiling at 90-95°C
4. Add dil NH_3 solution dropwise with stirring until $Mn_3(PO_4)_2$ ppt is formed.
5. Stop adding NH_3 soln. Continue heating and stir, ppt is formed ($MnNH_4PO_4 \cdot H_2O$) which is in crystalline state.
6. Allow the solution to stand at room temp for 2 hrs. Filter.
7. The ppt is taken in preweighed crucible (W_1) and wash with ammonium nitrate solution.
8. Dry under oven at 105-110°C and then undergo ignition at 900-1100°C. Cool it and weigh (W_2).

(7) The diff. ppt. gives the wt. equal of $Mn_2P_2O_7$

$$\% Mn = \frac{W_2 - W_1 \times G}{Wt\ of\ sample} \times 100$$

2 Mn / $Mn_2P_2O_7$. Mn / $MnNH_4PO_4$

Determination of alkalies:

Method: Volumetric method

Reaction: $NaCl + AgNO_3 \rightarrow NaNO_3 + AgCl\downarrow$

$KCl + AgNO_3 \rightarrow KNO_3 + AgCl\downarrow$

Reagents:

$BaCl_2$ soln, HF, H_2SO_4, $(NH_4)_2CO_3$, $AgNO_3$

Procedure:

(1) Collect 1g of iron ore sample in a beaker it is dissolved in 40ml HCl and few ml of HNO_3

(2) Evaporate to dryness and redissolve using HCl.

(3) Filter the solution and undigs ignition for residue.

(4) Filtrate is preserved.

(5) The ignited residue is treated with H_2SO_4 and HF and evaporate to dryness. and boil the residue with HCl.

(6) Add this solution to above (previous) filtrate. To this add $BaCl_2$ soln & filter.

$BaCl_2$ transforms alkali sulphates → alkali chlorides

$Na_2SO_4 \rightarrow NaCl$

$K_2SO_4 \rightarrow KCl$.

(7) Boil the filtrate & add $(NH_4)_2CO_3$ to ppt Fe → $Fe(OH)_3$, Ca & Mg, barium as carbonates ($CaCO_3$, $MgCO_3$, $BaCO_3$)

(8) Dilute with distilled water and allow

to settle. filter the solution.

(9) Collect the filterate and evaporate to dryness.

(10) Dilute with hot water & filter

(11) Filtrate is taken & is acidified with HCl. Heat the solution & ignite.

(12) Cool & weigh as NaCl & KCl

(13) These are titrated using silver nitrate solution using potassium chromate as indicator. (Endpt → Reddish brown ppt)

$$\% \text{ NaCl} = \frac{\text{Vol of } AgNO_3 \times \text{Conc of } AgNO_3 \times C}{\text{wt of sample}} \times 100$$

C = 0.05N $AgNO_3$ = x g of NaCl

$$\% \text{ KCl} = \frac{\text{vol of } AgNO_3 \times \text{Conc of } AgNO_3 \times C \times 100}{\text{wt of sample}}$$

C = 1 mL 0.05N $AgNO_3$ = x g of KCl

Determination of Carbon as Coke in blast furnace, Flue dust and Sinter.

Method : Gravimetric mtd

Procedure :

1. Collect 1g sample in 250 ml tall beaker
2. Diluted with or Moisten with 10 ml hot water
3. Add 0.7g NaF and boil until it dissolves
4. Add 50ml HCl solution. Shake gently and heat it for 20-30 min.
5. Dilute with 50 ml hot water. Again heat for 10 min and filter. ppt is taken in crucible
6. Wash several times with HCl and hot water
7. Evaporate to dryness on water bath
8. Cool and weigh.
9. loss in wt gives the percentage of carbon as coke.

Manganese ore

Manganese ore is principal raw material for determination of ferromanganese and electrolytic Manganese.

The constituents are SiO_2, BaO, Fe_2O_3, Al_2O_3, Mn, MnO_2, CaO, P, S.

Determination of SiO_2 and BaO:

Method: Gravimetry

Reaction: ① $FeSi + 6HCl \rightleftharpoons SiCl_4$ $\xrightarrow{HF/H_2SO_4}$ $SiF_4\uparrow$ "

$SiCl_4 \xrightarrow{H_2O} SiO_2 \cdot nH_2O \xrightarrow{\Delta}$

② $SO_4^{2-} + BaCl_2 \rightarrow BaSO_4$

Reagents: HCl, HF, H_2SO_4, NH_4OH.

Procedure:

① Collect 1g. of Manganese ore sample in a beaker. ~~Dilute this~~ Dissolve in 20ml HCl and heat the solution until it evaporates to dryness.

② The mass is again dissolved in HCl.

③ Take few ml of this solution and add 10 ml of H_2SO_4 and evaporate to dogeiss fumes.

④ Cool it and add 150 ml water & boil.

⑤ Allow to Stand for few hrs.

⑥ filter and Wash. Collect the filtrate and Preserved.

⑦ The ppt obtained is taken in crucible and undergo ignition and weigh the sample.

⑧ This weight represents both the wt of Crucible & the residues of SiO_2 & $BaSO_4$.

(a) SiO_2 determination

Ignited residue is taken and is treated with H_2SO_4 and HF solution.

→ The solution is heated until it expels SiO_2 as SiF_4.

→ Ignite the residue again & weigh the crucible

→ The loss in wt gives SiO_2 amount

$$\% Si = \frac{W_2 - W_1 \times C}{\text{wt of sample}} \times 100 \qquad C = Si/SiO_2$$

(b) BaO determination:

The residue left after removal of SiO_2 is collected and fused with 1g Na_2CO_3.

→ Extract the mass with dil HCl.

→ Add dil H_2SO_4 and adjust the acidity of solution with NH_4OH.

→ Allow to stand. Filter. Filtrate is preserved

→ The ppt obtained is taken in preweighed crucible (W_1).

→ Dried the ppt at 105–110°C & ignite.

→ Cool it and weigh as $BaSO_4$.

$0.6570 \times BaSO_4$

$$\% BaO = \frac{W_2 - W_1 \times C}{\text{wt of Sample}} \times 100$$

$C = BaO/BaSO_4$.

The filtrate obtained from BaO is added / combined to Main filtrate & is taken in 500 mL Measuring flask and make upto the Mark.

This filtrate solution is used for further determinations (Fe_2O_3, Al_2O_3, Mn, CaO, P, S, MnO_2)

Determination of Total Manganese

Method: Volhard's methods – Volumetric analysis

Principle:

(1) Volhards mtd is applicable only when Fe is removed as $Fe(OH)_3$ by ZnO.

(2) ZnO should free from $ZnCO_3$, Or else it will remove Mn as $MnCO_3$ along with $Fe(OH)_3$ and give low results of Mn.

(When neutral soln of $MnSO_4$ is treated with std $KMnO_4$, MnO_2 removes as PPt which indicates pink colour. The vol of $KMnO_4$ consumed gives amt of Mn present)

$$3MnSO_4 + 2KMnO_4 + 7H_2O \rightleftharpoons 5MnO_2 \cdot H_2O + K_2SO_4 + 2H_2SO_4$$

Reagents:

ZnO, ~~NaOH~~ $KMnO_4$, HNO_3.

Procedure:

(1) Collect filtrate from SiO_2 & BaO determination
(2) Heat the solution to boiling
(3) ZnO is added to solution in excess, Fe is removed as $Fe(OH)_3\downarrow$ (indicated by milkiness of upper layer of liq).

(*Here NH_4OH / NaOH are not used as precipitant instead of ZnO b'cos it precipitates Fe, Mn as hydroxides which lowers the result)

(4) To this solution add few drops of
(5) Filter the solution. Residue is rejected
(6) To the filtrate add few drops of HNO_3/H_2SO_4 and titrate the solution with std $KMnO_4$ solution.

(6) The end point shows the appearance of Pink colour.

Note: (HNO_3 is added before titration bcos it gather & settles MnO_3 ppt & helps in indicating the end pt sharply).

∴ The volume consumed by $KMnO_4$ gives the amt. of Mn present in sample

$$\% Mn = \frac{\text{Vol of } KMnO_4 \times \text{Conc of } KMnO_4 \times C}{\text{wt of Sample}} \times 100$$

C = 1 ml of 0.05 N $KMnO_4$ = x g of Mn.

SODIUM BISMUTHATE METHOD (Det of Mn).

Method: Mn can also be determined Volumetrically by Sodium bismuthate ($NaBiO_3$) mtd

Principle:

(1) $Mn(NO_3)_2 + NaBiO_3 + HNO_3$
(2) ‖ (7)
$HMnO_4 + Bi(NO_3)_3 + NaNO_3 + H_2O$
(permanganic acid)

(2) $HMnO_4 + FeSO_4 + H_2SO_4 \rightleftharpoons Fe_2(SO_4)_3 + MnSO_4 + H_2O$
(7) (7) (3) (2)

(3) $FeSO_4 + KMnO_4 + H_2SO_4 \rightleftharpoons Fe_2(SO_4)_3 + MnSO_4 + K_2SO_4 + H_2O$
(7) (7) (3) (2)

Reagents:
Std. ferrous ammo sulphate, Std KMnO4, HNO_3, $NaBiO_3$

Procedure:
(1) Collect filtrate from SiO_2 and, it is dissolved in 50 ml dil. HNO_3 in conical flask.
(2) Boil for 5 minutes. Cool by adding cold water
(3) Add about 1g Sodium bismuthate ($NaBiO_3$) and again boil for 5 min.
(4) There will be permanent pink colour due to Permanganic acid ($HMnO_4$) which indicates Complete Oxidation of Manganous salt.
* If ppt / colour is not obtained again add 0.5g more $NaBiO_3$ & boil for 5 min.

This preliminary oxidn is done to distroy any organic matter or any reducing substance would later react slowly with $KMnO_4$ & produce low results. *

(5) To this add Conc. solution of freshly prepared sulphurous acid until sol^n b'coms clear.
(6) Expel SO_2 by boiling. Cool the solution.
(7) Again add 0.5g Sod. bismuthate & stir the mix
(8) Add HNO_3 solution & filter.
(9) Wash the residue well with HNO_3 solution until washings are colourless.
(10) To this solution add known amt of ferrous ammo. sulphate from burette in excess. (This is indicated by disappearence of pink colour).
(11) Then this solution is back titrated with Std $KMnO_4$ solution until pink colour is obtained.

From Vol. of $KMnO_4$, amt of Mn present in sample can be determined.

$$\%\ Mn = \frac{\text{Vol of } KMnO_4 \times \text{Conc of } KMnO_4 \times C}{\text{Wt of Sample}} / 100$$

C = 1.0 ml of 0.05N $KMnO_4$ = x g of Mn.

Determination of MnO_2:

Method: Volumetric mtd

Reaction Involved:

$$MnO_2 + H_2C_2O_4 + H_2SO_4 \rightleftharpoons MnSO_4 + 2CO_2 + H_2O$$

$$H_2C_2O_4 + KMnO_4 + H_2SO_4 \rightleftharpoons MnSO_4 + K_2SO_4 + 10CO_2 + 8H_2O$$

Reagents:
Oxalic acid, H_2SO_4, $KMnO_4$.

Procedure:

① Filtrate is collected from SiO_2 / take 0.5g Ore sample in beaker.

② Add about 40 mL of 20% H_2SO_4 and add a known amt of Oxalic acid in excess.

③ Heat the solution and Mix well until it dissolves

④ Dilute it to 250 mL.

⑤ Take small portion, add H_2SO_4 solution, heat to about 60°C and titrate the soln with $KMnO_4$.

The vol consumed by $KMnO_4$ gives the amt of MnO_2.

$$\%\ MnO_2 = \frac{\text{Volume of } KMnO_4 \times \text{Con of } KMnO_4 \times C \times 100}{\text{Wt of Sample}}$$

C = 1.0 ml of 0.05N $KMnO_4$ = x g of MnO_2

CHROMITE ORE

Chromite $Fe.O.Cr_2O_3$ is the main source of chromium metal.

FeO, Cr_2O_3 are Major Constituents

Other Constituents are SiO_2, FeO, Al_2O_3, CaO, MgO

Determination of chromium :

Method : Volumetric method (Sod. peroxide mtd)

Principle :

Cr is determined by fusing the Ore with Oxidising flux (Na_2O_2) & titrating dichromate with $KMnO_4$.

Ore + Na_2O_2 $\xrightarrow{\text{fusion}}$ Conversion of →

Cr ⟶ Sod. chromate

SiO_2 ⟶ Sod. Silicate

Al_2O_3 ⟶ Sod. Aluminate

FeO ⟶ Fe_2O_3

Ca, Mg ⟶ CaO & MgO

When fused mass is dissolved in water, all constituents goes into solution, except Fe, Mg, Ca. The Soln is titrated with $KMnO_4$

$$Na_2Cr_2O_7 + 6FeSO_4 + H_2SO_4$$

$$\Downarrow$$

$$Cr_2(SO_4)_3 + Fe_2(SO_4)_3 + Na_2SO_4 + H_2O.$$

Reagents

Na_2O_2, $KMnO_4$, Ferrous-Amm. sulphate, H_2O_2

Procedure :

(1) Take finely ground 1g of ore sample And Mix thoroughly with 3-4g Na_2O_2 in Crucible.
(2) Cover the crucible with lid and fuse the Contents by slow heating & further 10-15 min.
(3) Cool the mass.
(4) And Again add 2g of Na_2O_2. Fuse it for further 10 min.
(5) Cool the crucible and is taken in beaker containing water (hot). Extract the fused mass
(6) Rinse well - Boil for 10 min to decompose H_2O_2 (formed by Na_2O_2 + water).
(7) Filter & cool
(8) Collect filtrate. To that add H_2SO_4 soln. Boil and add 5% KMnO4 solution until Pink colour persists.
* (KMnO4 is added to destroy H_2O_2 (formd by Na_2O_2 & water) If H_2O_2 is present, acidified soln of Sod. chromate will get reduced.
It is difficult to expell all H_2O_2 from Sod. chromate soln. So, the soln is acidified and any chromate reduced is oxidised by KMnO4). *
(9) Continue boiling and add 15ml HCl soln and water.
(10) Continue boiling until chlorine is given off
(11) Cool the soln.
(12) To this add excess of ferrous Amm. Sulphat (Kaoun ant) $FeSO_4(NH_4)SO_4 \cdot 6H_2O$ until yellow colour

disappears

(13) This solution is titrated back with std KMnO4 soln.

(14) The end pt will be pink colour.

∴ The vol consumed by FAS gives the amt of Cr present in Sample

$$\% Cr = \frac{\text{Vol of FAS consumed} \times \text{Conc of FAS} \times C \times 100}{\text{Wt of Sample}}$$

C = 1.0 ml of 0.05 N FAS = x g of Cr.

SiO_2, Fe_2O_3, MgO, CaO. Refer Iron Ore
Al_2O_3

ALUMINIUM ORE (BAUXITE).

Bauxite is the principal raw ore of aluminium. The constituents present in the aluminium ore are SiO_2, Al_2O_3, Fe_2O_3, TiO_2, MnO, P_2O_5, CaO, MgO, V_2O_5 and alkalies. Loss on ignition moisture content.

Determination of Vanadium:

Method: Gravimetric method.

Vanadates are precipitated by excess Silver nitrate solution in the presence of Sodium acetate. After boiling the precipitate consists of Silver orthovanadate.

$$2NaVO_3 + 2CH_3COONa + H_2O \rightleftharpoons Na_4V_2O_7 + 2CH_3COOH$$

$$Na_4V_2O_7 + AgNO_3 \rightleftharpoons Ag_4V_2O_7 + NaNO_3$$

$$Ag_4V_2O_7 + AgNO_3 + CH_3COONa + H_2O \rightleftharpoons Ag_3VO_4 + CH_3COOH + NaNO_3$$

Reagent
HNO_3
NH_3
Sodium acetate
N $AgNO_3$

Procedure:

(1) Collect 1g of finely ground aluminium ore and dissolve the sample in neutralised with HNO_3 (nitric acid) solution. (if the sample is in acidic form it is neutralised with aq NaOH)

(2) Boil the solution until it becomes yellow.

(3) Add dil NH_3 solution, the solution becomes decolourised.

(4) Add 5g of sodium ammonium acetate, cone NH_3 solution and then excess of $AgNO_3$ solution is added.

(5) Heat to boiling and then keep on steam-bath for 30 min.

(6) Dense brown precipitate of Silver vanadate is formed. Allow the ppt to settle.

(7) Collect it on a preweighed crucible (w.)

(8) Wash the precipitate with hot water and dried at 110 - 120°C.

[illegible] at 450°C.

$$\%V = \frac{W_2 - W_1 \times C}{\text{Wt of sample}} \times 100$$

$C = V/Ag_3VO_4$.

Determination of Zirconium:

Method: Gravimetric method.

Principle: Zirconium may be precipitated from hydrochloric acid solution with Mandelic acid ($C_6H_5CH(OH)COOH$) as Zirconium Mandelate $Zr(C_8H_7O_3)_4$ which is ignited & weighed.

$$ZrCl_2 + C_6H_5\text{-}CH(OH)COOH \longrightarrow Zr(C_8H_7O_3)_4$$

Mandelic acid. Zirconium mandelate

$\downarrow \Delta$ ignition

ZrO_2

Procedure:

(1) Take 1g of ore sample. The sample is dissolved in Hcl solution.

(2) or

→ Collect as filtrate from silica. To that add Hcl solution and dissolve completely.

→ To this solution add aq Mandelic acid solution and dilute to 100 mL.

→ Raise the temperature to 85°C and maintain the temperature for 20 minutes.

→ Precipitate is observed. And Allow the PPt to settle.

→ Filter the solution. The ppt is washed with hot solution containing 2% Hcl. and 5% Mandelic acid.

→ The Precipitate is dried and undergo ignition at the temp of 900-1100°C.

→ And Weigh the sample as $ZrO_2(W_2)$.

→ The difference in weight gives the amount of Zr in molecule.

$$\therefore \% Zr = \frac{\text{Wt}_2 - \text{Wt}_1 \times f}{\text{Wt of Sample}} \times 100$$

$$f = Zr/ZrO_2$$

Phosphate rock ore

Determination of Fluoride:

Method: Fluoride can be determine using Spectrophotometric method

Principle: Fluoride can be determined with thorium chloranilate in aq 2-methoxyethanol (Methyl cellosolve) at pH 4.5 under the absorbance 540nm.

→ $Th(C_6Cl_2O_4)_2 + 6F^- + 2H^+ \rightleftharpoons ThF_6^{2-} + 2HC_6Cl_2O_4$

(If water is solvent)

If Methylcellosolve is solvent

$Th(C_6Cl_2O_4)_2 + 2F^- + H^+ \rightleftharpoons ThF_2C_2O_4 + HC_6Cl_2O_4^-$

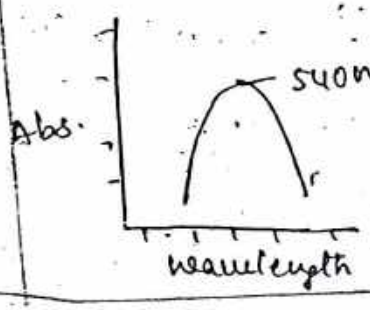
Reagents:

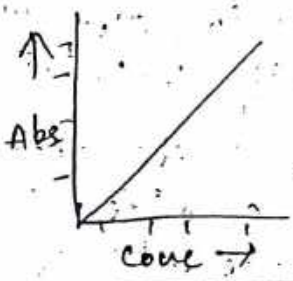
Methyl cellosolve (2-Methoxyethanol)
Thorium Chloranilate, pH 4.5, Standard fluoride sol

Procedure:

① Collect the sample from phosphate rock ore and prepare stock solution using distilled water / or collect filtrate from SiO_2 and neutralised with distilled water

3) To the solution add 25 ml of 2-methoxy-Methanol (Methyl cellosolve) and 10 ml of buffer (pH 4.5) solution in volumetric flask.
4) Again dilute the volume with distilled water.
4) And add 0.05g. thorium chloranilate
5) Shake the flask for 30 min.
6) The solution will be in orange coloured solution and is measured under Spectrophelometer at absorbance 540 nm.
7) Read it against Blank.
7) Draw the caliberation curve using standard fluoride solution.





Determination of chloride :

Method → Spectrophielometric method using Hg(SCN)$_2$ (Displacement rxn).

Principle →

This procedure depends on the displacement of thiocyanate ion from Mercury (II) thiocyanate by chloride ion in presence of Fe (III), a highly coloured $Fe(SCN)^{2+}$ (ferric thiocyanate) complex is formed and is measured under 460 nm.

$$2Cl^- + Hg(SCN)_2 + 2Fe^{3+} \rightleftharpoons HgCl_2 + 2[Fe(SCN)]^{2+}$$

The Intensity of colour is proportional to chloride ion in sample.

Procedure:-

① Collect filtrate from SiO_2 and is diluted
② using distilled water
③ To this solution add 2.0 ml of ammonium iron (III) sulphate ($Fe(NH_4)(SO_4)_2 \cdot 12H_2O$)
④ Mixwell. And add 2.0 ml of saturated solution of Mercury (II) thiocyanate in ethanol.
⑤ After 10 minutes Measure the absorbance of the sample at 460nm against blank in spectrophotometer.

The amount of chloride ion in sample corresponds to difference b/w two absorbances and which is obtained by calibration curve

→ Draw the calibration curve and using standard chloride solution and determine the amount of chloride ion.