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Manual of Procedure for

Chemical and Instrumental Analysis of

Ores, Minerals, Ore Dressing Products and Environmental Samples

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PREFACE

The chemistry of rock/ore is the key to understand the concentration of elements and presence of other associated elements. There is no doubt that chemical analysis reveals economic value of any mineral/rock.

The chemical analysis of samples shall guide and aid the future course of exploration with reference to the quantum, quality and the time frame. Chemical assay is also very important and helps the beneficiation engineers to plan their test work and do the required improvement during the beneficiation process. The chemical analysis of ore/processed products speaks of their suitability for various mineral based industries.

Ores and minerals have variety of elements and radicals, which offer interference with one another during analysis. The chemist has to choose the exact procedure of chemical analysis depending upon the nature of ore samples and radicals/elements to be analyzed. The choice of any analytical procedure or instrumental analytical techniques also depends on the concentration of elements in parts per million (PPM) or otherwise. Thus each procedure of chemical analysis has its own merits and demerits and selection of method is based on desired accuracy.

Instrumental analysis using instruments like XRF, AAS, ICPA, Ion-chromatograph, FTIR brought a modernization and sophistication to the analytical data. The analyst needs to develop techniques very carefully for the standardization and calibration of the instrument for obtaining the reproducibility and accuracy in the results.

The analysis of environmental samples for the various parameters in waste, water, drinking water, soil and ambient air help in preparing a baseline data and environmental management plans for the mines. The methods based on ISI procedures and using modern sophisticated instruments have been selected and mentioned in the manual.

Rapid and accurate analysis of samples holds the key to success in exploration, mineral based mining, marketing and assess quality of mineral based products.

This revised edition is brought for the industry.

(C.S.GUNDEWAR)
Controller General
Indian Bureau of Mines

Nagpur
Dated : 21st February, 2012

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1. Method of Analysis Using Wet Classical and Colourimetric Procedures

1.1 OPENING OF ORE/MINERAL SAMPLE

The chemical transformation of any ore/mineral sample into a desired form so as to facilitate analysis of its constituents is known as opening of the sample i.e., conversion of an ore or mineral sample into desired soluble or insoluble species. In simple words, opening of an ore is its dissolution in suitable solvent or flux depending upon the aim of analysis. Thus, opening of a sample is a very vital and important step in ore/mineral analysis. The separation of soluble and insoluble species should be near 100%. The exact choice of method for opening of an ore depends on the nature of the ore, the element of interest and its chemical properties. The selection of the appropriate method of sample decomposition is very important for correct analysis. To achieve this, an analyst should carefully take into account the chemical properties of various minerals present in the sample. Owing to the variable characteristics of the ore, it is not possible to have any one set procedure applicable to all samples. It is often necessary to combine two or more methods to effect the dissolution of an ore. There are mainly two methods to open an ore. They are (1) wet method & (2) dry method.

Wet method constitutes the digestion of an ore sample with an acid or a mixture of acids to convert the complex ore mineral into simple chemical compounds. The action of an acid or a mixture of acids is supplemented by heat and pressure. Heat and pressure hasten the dissolution rate. This is normally preferred over dry method due to its simplicity and it requires less attention, moreover, the dissolving media least affects the vessel used.

Dry method constitutes the fusion of an ore with a solid or mixture of solids to convert complex minerals compound into simple chemical compounds. The reaction is effected by melting the mass at elevated temperature. The fusion is carried out in variety of crucibles made of platinum, gold, nickel, iron, zirconium, palladium, silica, porcelain etc. There are numbers of chemical compounds used for fusion. The choice of fusion mixture depends on the nature of the ore to be fused and the nature of the final product needed for further analysis.

Before entering into the further details of use of wet and dry methods, it is necessary to categorize the ore samples. On the basis of their chemical composition and chemical properties, the categorization makes the opening of an ore easy and logical. Following are the main categories of ores on the basis of their chemical composition.

1. Carbonates
2. Sulphides and Pyrites
3. Oxides
4. Sulphates
5. Silicates

6. Phosphates
7. Spinel (mixed oxides)

On the basis of chemical properties of an ore, various acids, combination of acids and acids with some suitable salts are generally employed for dissolution of an ore sample. Choice and reactivity of various reagents are given here:

S.No	**Reagent**	**Material to be treated**
1.	Water	Alkali salts
2.	HCl	Carbonates and oxides ore of Fe, Ca, Mn, Mg, P, Sn, Ti, Zn etc., sulphides of various metals
3.	HCl with Oxidizing agent	Sulphides/pyrites, ores of Cu, Pb, Mo, Zn, Ni, Fe, As, etc.
4.	Nitric Acid	Ores of Cd, Cu, Mo, Co, Ni, etc.
5.	Aqua regia	Ores of Cd, Mg, Rh, W, etc.
6.	H_2SO_4	Ores of Al, Be, Mn, Pb, Th, Ti, V, etc.
7.	HF (with HCl, $HN0_3$ or H_2SO_4)	Silicates where SiO_2 is not to be determined.
8.	Perchloric Acid	A powerful oxidizing and also a dehydrating agent when hot and concentrated. The solubility of the majority of the perchlorates in water makes the acid a very desirable solvent.
9.	H_2O_2 & HCl	One of the most promising combination of reagents
10.	Acetic acid (10%)	For selective dissolution of carbonates
11.	Ammonium acetic solution	For dissolution of gypsum, $PbSO_4$ etc.
12.	Alcohol	Used for separation of $MgSO_4$ and $CaSO_4$
13.	Sugar solution	Estimation of CaO in cement, quick lime etc.
14.	H_3PO_4	In phase analysis of free silica to dissolve silicates but not quartz.
15.	H_3PO_4& H_2SO_4	To dissolve fused Al_2O_3 and chrome ores.

Fusion, dry methods, remains as popular as wet acid decomposition, in spite of their apparent disadvantages such as increased solid contents in the test solution, greater reagent requirement, more problems with reagent blank. In making fusion, the sample is well mixed with six to twenty times its weight with fusion mixture and placed over a thin layer of the flux in the crucible and then covered by a lid of the material as that of the crucible. In case of refractory oxides, adding a small piece of filter paper to the molten mass assists decomposition.

Fluxes can be categorized into the following main categories on the basis of their chemical properties.

1.	Acidic flux	:	$KHSO_4$, $K_2S_2O_7$, $NaHSO_4$, $Na_2S_2O_7$, etc.
2.	Basic flux	:	Na_2CO_3, K_2CO_3, KOH etc.
3.	Oxidizing flux	:	Na_2O_2, KOH – KNO_3 etc.
4.	Reducing flux	:	Na_2CO_3 – C

Acidic fluxes are commonly used for dissolution of basic oxides, wolframite, powellite, sulphides/pyrites etc.

Basic fluxes are commonly used for dissolution of acidic oxides, silicates, amphoteric oxides etc.

Oxidizing fluxes are employed for two reasons; firstly, their dissolution capacity is higher than acidic and basic flux, secondly for selective conversion of element of interest into higher oxidation state like sulphide to sulphate, chromic oxide to chromate.

Reducing fluxes are generally employed for converting element of interest into lower valency state, like conversion of sulphates to sulphides.

Choices and reactivity of various fluxes are given below:

S.No.	**Reagent/Flux**	**Material**
1.	Na_2CO_3	Silicates of Al, Fe, Ca, Cr etc, halides of Ag, sulphates of Ba & Pb.
2.	Na_2CO_3 & K_2CO_3	Silicates of Al, Fe, F, N, Se, Te, etc.
3.	Na_2CO_3 with oxidizing agent	Ores of Sb, As, Cr, Fe, Mo, V, Zr, sulphides, pyrites etc.
4.	Na_2O_2	Ores of Sb, As, Cr, Mo, Ni, V, Sn etc. in sulphide for sulphur determination.
5.	$KHSO_4$, $K_2S_2O_7$	Ores of Al, Sb, Cu, Cr, Co, Fe, Mn, Ni, Rh, Ta, Ti, W etc.
6.	NaOH, KOH	Oxidized Sb ore, ores of Cr, Sn, Zn, Zr, sulphides and sulphates etc.
7.	$CaCO_3 + NH_4Cl$ (J.Lawrence Smith method)	Estimation of alkalies in silicates
8.	$NH_4Cl + NH_4\ NO_3$ (Solid aquaregia)	For dissolution and oxidation of sulphide and pyrite.
9.	$NH_4NO_3 + (NH_4)_2SO_4$	Dissolution of sulphide and pyrites.
10.	Eshka Mixture Na_2CO_3 + MgO	For sulphur determination in coal sample.
11.	Na_2CO_3 + C	Used for reduction of sulphates to sulphides.
12.	Lithium Borate	Promising for various silicates
13.	Na_2CO_3 + Borax	Estimation of silica in sample containing fluorine.

Broad outline of the ores categorized for chemical analysis can be summerised as follows:

All carbonates are attacked by mineral acid. Limestone, dolomite etc. are treated with concentrate hydrochloric acid. Carbonatic material passes into solution and silicate and other insoluble material are left as insolubles. Insolubles are then treated with hydrofluoric acid, where silica is hydrofluorised. The remaining unattacked material is fused with suitable flux ($K_2S_2O_7$, Na_2CO_3 etc.) and then extracted in mother liquor.

Most of the hydrated oxides (Al_2O_3 $2H_2O$, Al_2O_3 H_2O etc.) and some other oxides are soluble in concentrated mineral acid; their solubility increases with degree of hydration. Higher the degree of hydration greater is the solubility. Hence goethite is more easily soluble than hematite or magnetite. Similarly gibbsite is more easily soluble than bohemite or diaspore.

Most of the phosphates are easily soluble in mineral acids. Normally a phosphate sample is dissolved in concentrated hydrochloric acid (with little HNO_3). Sulphuric acid must not be used, as the presence of sulphate ion is not desired in Wilson method of phosphate estimation.

Mineral acids attack all sulphides. Pyrites are resistant to hydrochloric acid but presence of nitric acid or sulphuric acid helps their dissolution**.**

Analysis of silicate is most complicated as the solubility of silicate ranges from watersoluble (sodium, potassium silicate) to HF resistant (magnesium silicate). While analyzing silicate, its solubility is taken into account, silicates which contains a high portion of bases such as calcium, copper, zinc etc. are decomposed by strong acids such as HCl. Clay, wollastonite etc. are attacked by concentrated hydrochloric acid and silica separates from the matrix. Silicates, which are acidic in nature, are only partially attacked by mineral acid and hence they are better analysed after fusing with suitable flux. If silica is not to be determined, a mixture HNO_3, HF and perchloric acid dissolves the silicate completely. Alternatively, a mixture of NH_4F and hydrochloric acid can be employed for dissolution of silicate rock.

Decomposition is generally hastened by using very finely ground sample (-200 mesh). Acids should never be added to a dry powder because of danger of loss due to ferocity of the reaction. The sample should be moistened with water, the acid is added cautiously and the covered container allowed to stand without additional heating till the completion of initial reaction.

This manual deals with procedures adopted by/evolved in Chemical analysis Laboratory of Indian Bureau of mines for analysis of various ores, minerals, ore dressing products, etc. Preparation of stock solution and determination of silica has been described ore/mineral-wise highlighting the special treatment or attention to be given in respect of certain radicals in the ore.

Following pages deal with determination of the content of common elements (major or minor) present in the stock solution**.**

1.2 DETERMINATION OF MAJOR AND MINOR CONSTITUENTS FROM THE STOCK SOLUTION

1.2.1 Major Elements

1.2.1.1 Iron (Fe) – (Dichromate method)

Pipette out 50 ml from the main stock solution into a 250 ml beaker. Add 2-3 drops of methyl orange (very dilute solution) to impart a very faint red colour to the solution. Add 2 g ammonium chloride. Stirr and dissolve the solids. Precipitate mixed oxide (R_2O_3) by dropwise addition of dilute ammonia till the colour of indicator turns yellow. Add 2-3 drops in excess. Boil the content on burner. Cool and filter through Whatman 41 filter paper. Wash the precipitate and beaker 5-6 times with hot water. Preserve the filtrate for estimation of CaO and MgO. Transfer the precipitate carefully with jet of hot water into the original beaker. Dissolve the precipitate in concentrated hydrochloric acid. Wash the sides of the beaker. Now heat the beaker to 80-90^{o}C on burner (avoid boiling) and add 10% stannous chloride solution dropwise with constant stirring to reduce iron. Yellow colour of ferric chloride disappears due to conversion to ferrous ion. Add 1-2 drops of stannous chloride in excess. Cool the solution in cold water. Add 10 ml mercuric chloride solution and stir. A silky white precipitate of mercurous chloride will appear. If the precipitate found is black, discard the solution and repeat the process with new aliquot. The black colour indicates the reduction of mercurous chloride to elemental mercury, which adds inaccuracies to the determination. Add 10-15 ml sulphuric-phosphoric acid mixture and dilute to about 150 ml. Add 2-3 drops of barium diphenylamine sulphonate indicator solution. Titrate this against standard dichromate solution with constant stirring till a constant stable violet colour appears. Colour changes from dirty green to violet. Avoid use of excess of indicator as it imparts intense dirty green colour near the end point and confuses the actual end point.

$$
\begin{aligned}
1 \text{ ml } 1 \text{ N } K_2Cr_2O_7 &= 0.05585 \text{ g Fe} \\
&= 0.07185 \text{ g FeO} \\
&\equiv 0.07985 \text{ g } Fe_2O_3
\end{aligned}
$$

1.2.1.2 Calcium Oxide (CaO)-EDTA (Complexometry) Method

Divide the filtrate of iron estimation (1.2.1.1) into two parts. One is used for estimation of calcium and other is preserved for estimation of MgO.

Take solution for CaO estimation in 250 ml beaker. Add 2-3 drops of tri-ethanol amine and stir. Now add a pinch of hydroxylamine hydrochloride or ascorbic acid. Add 50 ml of 20% KOH solution. Add 5-6 drops of Patton and Readers indicator. The indicator will impart rose red colour to the solution. Titrate this against standard EDTA solution. Colour changes from rose red to blue. Sometimes 0.5-1 ml of 10% potassium cyanide solution is added to mask heavy metals (especially in case of Cu-Pb-Zn ores). Use of cyanide should be avoided and should only be used with care and caution in case of need. Cyanide must be used in alkaline media only. The excess of cyanide in waste must be destroyed with bleaching powder before it is disposed to sewage.

1 ml of 1 M EDTA ≡ 0.05608 g of CaO

Oxalate Method (Volumetry)

The silica and mixed hydrated oxides are removed. The solution is acidified with hydrochloric acid and calcium is precipitated as calcium oxalate. The precipitate is filtered, washed, dissolved in hot dilute sulphuric acid and titrated against standard potassium permanganate solution to pink colour.

Take the ammonical filtrate from the mixed oxide precipitation in a 500 ml beaker; acidify the solution with hydrochloric acid using methyl red as indicator. Add about 0.5 gm of ammonium oxalate and stir well. Make the solution ammonical and boil for about 10 minutes. Remove from the flame and allow the precipitate to settle for about one hour. Filter through No.40 Whatman filter paper and wash the residue with hot water till free from oxalate (test the filtrate with a drop of dilute permanganate solution and a drop of dilute sulphuric acid). Collect the filtrate and the washing for the determination of MgO. Spread out the filter paper containing the precipitate and wash out the precipitate into the beaker with water. Add about 25 ml of 1:1 sulphuric acid and warm the solution (70 to 80°C), titrate with standard permanganate solution till a permanent pink colour persists. Calculate % CaO as follows

$$\text{CaO \%} = \frac{A \times B \times 0.028 \times 100}{C}$$

Where

A = volume in ml. of standard permanganate solution used
B = normality of permanganate solution, and
C = weight in gm of the sample representing the aliquot taken

Reactions involved

1. $Ca^{++} + C_2O_4^{-} = CaC_2O_4$
2. $CaC_2O_4 + 2H^{+} = Ca^{++} + H_2C_2O_4$
3. Potassium permanganate in the presence of dil. sulphuric acid oxidizes oxalic acid to carbon dioxide and water.

The following reaction takes place –

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 = 10CO_2 + 8H2O + K_2SO_4 + MnSO_4$$

The ionic reaction is –

$$2MnO_4^{-} + 5C_2O_4^{--} + 16H^{+} = 2Mn^{++} + 10CO_2 + 8H_2O$$

1.2.1.3 Magnesium Oxide-EDTA Method (Complexometry)

Take part of the iron estimation filtrate preserved for estimation MgO in 250 ml beaker. Add 2-3 drops of triethanol amine and stir. Now add a pinch of hydroxylamine hydrochloride or ascorbic acid. Add 50 ml, 10-pH ammonia-ammonium chloride buffer. Add 5-6 drops Eriochrome Black T indicator solution.

The indicator will impart brilliant red colour to the solution. Titrate this against standard EDTA solution. Colour changes from red to blue. This titration estimates calcium and Magnesium together. Find magnesium equivalent EDTA by subtracting volume required for CaO determination. Sometimes 0.5-1 ml of 10% potassium cyanide solution is added to mask heavy elements (especially in case of Cu-Pb-Zn ores). Use of cyanide should be avoided and should only be used with care and caution in case of necessity.

Caution:

Cyanide must be used in alkaline media only. The excess of cyanide in waste must be destroyed with bleaching powder before it is disposed to sewage.

1 ml 1 M EDTA ≡ 0.04030 of MgO

Pyrophosphate Method (Gravimetry)

Determination of MgO

Outline

When a cold acid solution of magnesium is treated with an excess of diammonium hydrogen phosphate and then excess of ammonia solution is added. Magnesium ammonium phosphate hexahydrate $MgNH_4PO_4.6H_2O$ is precipitated at room temperature.

The magnesium ammonium phosphate hexahydrate is ignited at 1000°C to 1100°C to magnesium pyrophosphate ($Mg_2P_2O_7$).

Procedure

Take the filtrate from the precipitation of calcium oxalate in a 500 ml beaker. Add 50 ml nitric acid and 20 ml. conc. hydrochloric acid and boil vigorously to destroy the organic salt. When the material is nearly dry, add 10-ml. conc. hydrochloric acid and 100 ml. water and boil. If the solution is not clear, filter through No.40 Whatman filter paper and wash the residue with hot water. Discard the residue and proceed with the filtrate. Add about 0.5 gm. of diammonium hydrogen phosphate $(NH_4)_2HPO_4$ and stir well to dissolve the phosphate. Add a few drops of methyl red indicator. Add conc. ammonia solution slowly, while stirring, until the indicator turns yellow. Continue to stir the solution for 5 minutes, adding ammonia solution drop wise to keep the solution yellow, and finally add 5 ml. of conc. ammonia solution in excess. Allow the solution to stand in a cool place overnight. Filter through No.40 Whatman filter paper. Wash the precipitate on the paper with cold 0.1% aqueous ammonia solution until free from chloride ions.

Remove the precipitate into a previously weighed platinum or porcelain crucible. Char the paper slowly and burn off the filter paper at a low heat and then ignite to a constant weight in an electric muffle furnace at 1000 to 1100°C and cool in a desiccators weigh and find out the weight of the residue.

Calculate the percentage of MgO from the factor:

$$Mg_2P_2O_7 \times 0.3623 = MgO$$

$$MgO\ \% = \frac{W_1 \times 0.3623 \times 100}{W_2}$$

Where –

W_1 = weight of the $Mg_2P_2O_7$ in gm. and

W_2 = weight in gm. of the sample represented by aliquot.

Reactions involved

1. $Mg^{++} + HPO^{--}_4 + NH_4^+ + OH^- = MgNH_4PO_4 + H_2O$
2. $2MgNH_4PO_4 = Mg_2P_2O_7 + 2NH_3 + H_2O$

Precautions

1. Precipitation should be done in an excess of ammonia since the precipitate has a tendency to dissolve in water (56 mg. Per 1000 ml at 20°C).
2. The precipitate should be washed with ammonical water to avoid solubility.
3. Since there is a tendency of coprecipitation, if time permits, the magnesium ammonium phosphate precipitate should be dissolved in hydrochloric acid and reprecipitated.

1.2.1.4 Alumina (Al_2O_3) -(EDTA Complexometry Back Titration)

Pipette out 50 ml. aliquot from the main stock solution in some beaker. Take 50-75 ml 10% NaOH solution in another 250 ml beaker. Neutralize the aliquot with 10% NaOH solution to a tea red colour. No precipitate of iron should appear. Transfer this to 10% NaOH solution, taken in other beaker with constant stirring. Wash the beaker with hot water to transfer all contents. Add a few drops of bromine water and a pinch of sodium carbonate to this. Boil the content on a burner. Cool and filter this through Whatman 41 filter paper with little filter paper pulp in 500-600 ml beaker. Wash the residue 5-6 times with hot water. (residue can be used for estimation of iron, calcium and magnesium after dissolving in hydrochloric acid. But, as per the experience of Indian Bureau of Mines analytical laboratory, the estimation is not very accurate). Acidify the filtrate with dilute hydrochloric acid with gradual addition. Precipitate of aluminium hydroxide will appear. Dissolve this with a drop of hydrochloride acid. The solution should be clear (actually this is the catch of pH required for titration). Add measured excess of EDTA solution to this. (Normally 25 ml of 0.05 M EDTA is added for estimation of Al_2O_3 in bauxite, clay, kyanite etc. and 10 ml. of 0.02 M EDTA is added for estimation of Al_2O_3 in iron ore, manganese ore, limestone etc.). Boil this. Cool this and adjust pH to 5.5 pH HCl and NaOH (or NH_3). Add 50 ml, 5.5 pH sodium acetate buffer. Add 5-6 drops of xylenol orange indicator. The indicator will impart golden yellow colour to the solution. Titrate this against (0.05 M or 0.02 M as the case may be) standard zinc acetate solution. Colour changes from yellow to orange red. The colour should be observed on the rim of the titrating solution. This is a back titration technique. Find zinc acetate equivalent for the volume of standard EDTA added. Find the amount of standard EDTA (or equivalent zinc acetate) consumed by aluminium ion for complexion.

1 ml 1 M EDTA ≡ 1 ml 1 M Zn-Acetate ≡ 0.05098 g Al_2O_3

Note: Zn interferes in this estimation. A modified method for estimation of zinc and aluminium together is given below.

Al_2O_3 and Zn (EDTA Complexmetry – back titration)

Follow the procedure given above under Al_2O_3 in toto. The first equivalence point will indicate the total amount of Al_2O_3 and zinc. Now add 1-2 g. of sodium fluoride to the solution after first titration. Boil the solution. Fluoride will complex aluminium ion and release equivalent amount of EDTA from Al-EDTA complex. Cool the solution. Titrate this against standard zinc acetate solution. Colour changes from golden yellow to orange red. Find the volume of EDTA required for complexing Zn ions.

1 ml 1M EDTA = 1 ml 1 M Zn-acetate = 0.06537 g Zn

Note: If only Zinc is to be estimated, Aluminium can be masked with Sodium fluoride or Ammonium bifluoride at first boiling stage and thus only Zinc will complex with EDTA.

1.2.1.5 Zinc (Zn)- (EDTA Complexometry – Back Titration)

Follow the procedure given above under Al_2O_3 in toto. The first equivalence point will indicate the total amount of Al_2O_3 and zinc. Now add 1-2 g. of sodium fluoride to the solution after first titration. Boil the solution. Fluoride will complex aluminium ion and release equivalent amount of EDTA from Al-EDTA complex. Cool the solution. Titrate this against standard zinc acetate solution. Colour changes from golden yellow to orange red. Find the volume of EDTA required for complexing Zn ions.

1 ml 1M EDTA ≡ 1 ml 1 M Zn-acetate ≡ 0.06537 g Zn.

Note: If only Zinc is to be estimated, Aluminium can be masked with Sodium Fluoride or Ammonium bifluoride at first boiling stage and thus only Zinc will complex with EDTA. Hence, Zinc can be estimated by direct titration at 5.5 pH. In this titration colour changes from wine red to golden yellow.

1.2.1.6 Manganese (Mn) (Volhard's method)

Pipette out 25 ml solution in 500 ml conical flask. Boil this and remove free chlorine. Dilute the volume to 150 ml with demineralised water. Add 5-6 g of zinc oxide. Shake vigorously. Heat this on burner to near to a boiling point (avoid boiling). Titrate this against standard potassium permanganate solution to a permanent pink colour. To observe the colour change the flask should be kept in slanting position and the insoluble should be allowed to settle and observe the colour in clear solution. Best is to run a control reading to locate the probable end point and finish the second/parallel titration to an exact end point.

1 ml 1 N $KMnO_4$ ≡ 0.01648 g of Mn

The reactions involved are

$$3Mn^{2+} + 2MnO_4 + (X+2)\ H_2O = 5MnO_2\ XH_2O + 4H^+$$

Notes on successful performance of Volhard's method

There is much criticism about the use of Volhard's method but in the Ore Dressing Laboratory of Indian Bureau of Mines, this process has been in practice for many years and the results obtained are quite reliable and satisfactory.

The following precautions are needed for the successful application of the method.

1. The titration is made quickly and the solution is not allowed to cool below 80°C during titration.
2. The permanganate causes formation of precipitate, which obscures the end point. A drop of HNO_3 makes the precipitate to settle quickly. The end point can be easily observed if the conical flask is kept in a slanting position on a stand.
3. Avoid boiling of the solution while titrating as it may destroy the permanganate colouration.
4. A chloride, sulphate or nitrate solution may be used for the determination of manganese but the amount of permanganate used will vary in each case. In fact many factors influence and the method is reported to be only empirical. The permanganate must be standardized against a similar ore or steel of known manganese content. (Ref.pp. 175 and 176 – Advanced Quantitative Analysis – LA companion Volume to Elementary).

1.2.1.7 Titanium Dioxide (TiO_2) – Ferric Ammonium Sulphate Titration Method (Volumetric)

Pipette out 50 ml aliquot into a 500 ml conical flask; add 25 ml concentrated hydrochloric acid. Add a strip of aluminium foil to the flask (nearly 2 g). Digest this on burner in presence of carbon-di-oxide. Boil at least for 30 minutes. All the time a slow stream of CO_2 must be maintained. Remove the flask from the heat. Cool this in cold water (preferably ice cold water) and slow current of CO_2 should be maintained during the process of cooling. Wash the side of conical flask. Add 5 ml. Ammonium thiocyanate solution. Titrate this quickly with standard ferric ammonium sulphate solution to a faint red colour. Run a blank and deduct this reading from the main reading.

1 ml 1N ferric ammonium sulphate ≡ 0.08 g TiO_2

1.2.1.8 Phosphorous Peroxide (P_2O_5) (Wilson Method –Quinoline Phospho Molybdate Method)

Dissolve 0.05 – 0.2 g of sample (0.05 for phosphorite, apatite etc., high P_2O_5 and 0.2 g for iron ore, manganese ore etc. with low P_2O_5) in 25-concentrated hydrochloric acid and few drops nitric acid (to convert meta phosphate to ortho phosphate) in 500-ml. conical flask. Cool the content. Neutralise the acid with 10%

NaOH solution. Redissolve the precipitate formed in dilute hydrochloric acid. Use litmus paper for indication. Add about 5 ml dilute hydrochloric acid in excess. Dilute the solution to 150 ml with DM water. Add a pinch of citric acid. Heat this to boiling on a burner. Add 30 ml citromolybdate solution, again heat it to boiling and add 25 ml. Quinoline hydrochloride solution very slowly with constant stirring. Boil this for 5-10 minutes. Cool this in cold water bath. Allow the precipitate to settle for 1-2 hours. If time permits, it is better to keep it overnight. Collect this precipitate on a pad of filter paper pulp under suction. Wash the conical flask thoroughly with cold water and transfer this to the precipitate collected on the pad. Wash the precipitate 8-10 times with cold water (till it is free from acid). Transfer the precipitate along with filter paper pad to the original flask. Add 50 ml DM water. Add known excess of 0.1 N NaOH solution to dissolve the yellow precipitate of quinoline phosphomolybdate completely. Add 2-3 drops of phenolphthalein indicator. Titrate this against standard hydrochloric acid solution (0.1 N) to a colourless end point.

1 ml 1 N HCl ≡ 0.001193 g of P ≡ 0.002733 g of P_2O_5

NB: Phosphorous can be estimated from R_2O_3 precipitation as R_2O_3 carries almost all P_2O_5 along with it, to ensure complete precipitation of P_2O_5 add 1-2 drops of concentrated ferric chloride solution before P_2O_5 precipitation. Dissolve R_2O_3 in HCl and proceed to precipitate P_2O_5 as detailed above.

1.2.1.9 Copper (Cu)-Copper (Sodium Thiosulphate titration)

Take 50 ml aliquot for copper estimation expel all nitrate, if present, either by treatment with urea with constant boiling or by fuming the mass with dilute sulphuric acid. The latter is more preferred as the nitrates are completely expelled out from the solution. Therefore, the stock solution is preferably prepared after fuming with sulphuric acid and extracting the mass in dilute sulphuric acid and water.

Neutralize the aliquot with dilute ammonia to neutralize all mineral acid. Add 8-10 ml of glacial acetic acid. Add 2.3 g of sodium fluoride. Boil this and cool in water bath. Add approx. 2-3 g potassium iodide and titrate the liberated iodine with standard sodium thiosulphate solution. Add starch near the end point. Finish to a colourless end point. Colour changes from blue to colourless.

1 ml 1 N $Na_2S_2O_3$ ≡ 0.06357 g of Cu.

The copper present in minute quantities in tailings, etc. is determined by the spectrophotometric method. The limit of Cu for this method is 0.01 to 0.15%.

Zn (Urea Hydrolysis method) (EDTA-Complexometry)

Take 50 ml aliquot in 250 ml beaker and neutralize the acid with dilute ammonia (precipitate should not appear). Add 2 g of urea and boil vigorously, check the pH of the solution continuously with pH paper. Adjust the pH to about 5. Remove the beaker from the flame. Wash the sides of the beaker with water. Cool this in cold water. Filter this through Whatman 41 with little filter paper plup. Wash the residue 5-6 times with hot water. Collect the filtrate in 400 ml beaker. Add 0.5 – 1.0 g. Ascorbic acid. Dissolve the solid. Now add 0.5-1 g. thiourea. Again dissolve all solids. Add 50 ml, 5.5 pH, sodium acetate buffer. Add 2-3 days of xylenol orange indicator. Indicator will impart purple red colour to the solution. Intensity will depend on the quantity of Zn in the solution. Titrate this against standard EDTA solution. Colour changes from purple red to golden yellow. Add a pinch sodium fluoride to avoid inference of alumina, if left unprecipitated by urea, with the end point.

1 ml 1M EDTA $\equiv$ 0.06537 g of Zn.

1.2.1.10 Lead (Pb) - (EDTA–Complexometry)

Separate Pb from other element by conversion to sulphate. Take 50 ml aliquot add 5 ml dil. sulphuric acid fume of the content. Wet the mass left with dil. H2SO4 and add 50 ml. Water. Boil this on burner. Filter this through Whatman 40. Wash the precipitate with hot water containing 5% sulphuric acid. Transfer the filter paper along with precipitate to the original beaker. Add 100 ml, 5.5 pH, ammonium acetate – acetic acid buffer. Boil this, cool this in water bath. Add a pinch of ascorbic acid and a pinch of thiourea. Dissolve the solids. Add 25 ml. Sodium acetate 5.5 pH buffer. Add 2-3 drops of xylenol orange indicator. Titrate this against standard EDTA solution. Colour changes from purple red to golden yellow.

1 ml 1 M EDTA $\equiv$ 0.2072 g. of Pb

1.2.2 MINOR ELEMENTS

1.2.2.1 TiO_2 & V_2O_5 (Hydrogen Peroxide method)

Titanium and vanadium both forms yellow coloured complex with hydrogen peroxide. Chloride ion and chlorine affects the colour of the complex, therefore all chlorides must be expelled before the colour is developed.

Procedure: Take 25 ml. aliquot in 250 ml beaker, add 1-2 ml. dil. Sulphuric acid and fume off the content on hot plate. Moisten the mass with dilute sulphuric and 50 ml. DM water. Boil the content. Filter if there is any turbidity. Add 5 ml. dilute sulphuric acid and 5 ml. ortho-phosphoric acid. Add 10 ml. (1:1) H_2O_2. Yellow colour of titanium complex will appear. Make up the volume to 100 ml. in volumetric flask. Measure the absorbance at 410 nm. This measurement will give the quantity of TiO_2 and V_2O_5 together. Add a pinch of sodium fluoride in the volumetric flask of titanium-peroxide complex, shake vigorously for few minutes filter through dry filter paper. Measure the absorbance at 410 nm. This colour will correspond to V_2O_5 content. Find TiO_2 by difference. If V_2O_5 is absent or negligible, the original reading (before adding sodium fluoride) of absorbance should be taken for finding equivalent of TiO_2 content.

Graph for TiO_2 estimation: Fuse 0.1 g of pure TiO_2 with potassium pyrosulphate (approx. 1 g.) in silica crucible. Extract the mass in 5 ml (1:1) sulphuric acid and 50 ml. DM water. Cool this and make up to 100 ml. in volumetric flask. Now each ml. of this solution will be equivalent to 1 mg. of TiO_2. Take out 1 ml, 2 ml,5 ml, 6 ml, 7 ml, 9 ml, 10 ml, aliquot and develop colour of Titanium-hydrogen peroxide complex at described above. Measure the absorbance and plot the graph.

1.2.2.2 Manganese (Mn) (Periodate Oxidation Method)

Determination of minute amounts of manganese (Per-iodate method) (Spectrophotometry)

Method

The sample is decomposed with hydrochloric and nitric acid and fumed with sulphuric acid. Phosphoric acid is added to complex the iron. Potassium periodate is added and boiled to develop permanganate colour. Manganese is determined spectrophotometrically at 545 nm or with a green filter.

Procedure

Take 0.5 gm of the sample in a beaker, add 10 ml. conc. hydrochloric acid and digest over a hot plate. Filter through No.40 Whatman filter paper. Wash the residue with hot hydrochloric acid. Burn off the filter paper in a platinum crucible, add a few drops of sulphuric acid and 5 to 10 ml. hydrofluoric acid, evaporate and fume off sulphuric acid. Dissolve the residue in hydrochloric acid, and add to the main solution.

Add 5 to 10 ml. sulphuric acid and 20-ml. nitric acid to the solution of the sample and evaporate to dryness. Thus, all chloride ions should be removed. Add 50 ml. water and heat until all ferric sulphate has been brought into solution. Filter off any suspended matter, add 5 to 10 ml. manganese-free phosphoric acid to the filtrate, and mix. The solution should be colourless.

Add 1 gm. of potassium periodate and heat to boiling (If there is any delay in the appearance of permanganate colour, the presence of chloride ions is indicated, and add more periodate). Take the solution in a 100 ml. volumetric flask and measure the optical density at 545 nm. Compute the percentage of manganese from the calibration graph prepared with a standard solution.

The reactions involved –

$$2Mn^{++} + 5IO_4^{-} + 3H_2O = 2MNO_4^{-} + 5IO_3 + 6H^{+}$$

Note:

1. It has been shown that with a low concentration of manganese, an acidity of 2 N, i.e. 5 to 6% by volume of sulphuric acid is ideal.
2. In this method Phosphoric acid decolorizes ferric iron by complex formation and prevents precipitation of periodate or iodates of manganese.
3. applicable for samples containing a low amount of manganese (0.02 to 3%).

Reference

E.B.Sandell, Colorimetric Determination of Traces of Metals, Third Edition, Inter Science Publishers, 1959, pp 609.

1.2.2.3 Copper (Spectrophotometric)

Decomposition of the sample

Take 0.5 gm. of the sample in a 250-ml. beaker, add 25-ml. conc. hydrochloric acid and digest for some time over a hot plate. Add 10 ml. conc. nitric acid and digest, when the reaction subsides, add 5 ml. of 1:1 sulphuric acid. Fume and dry. Remove from the hot plate. When cool, add 5 ml. conc. hydrochloric acid and nearly 100 ml. distilled water and boil and filter through No.40 Whatman filter paper. Wash the residue with hot water acidified with hydrochloric acid. Take the filtrate in a 250 ml. volumetric flask and make up to the volume.

Procedure

Take an aliquot equivalent to 0.1 gm. in a 250-ml. beaker; add 5 ml. 10% hydroxylamine hydrochloride solution and 5 ml. 10% tartaric acid solution. Adjust the pH at 5 to 5.5 with AR ammonium hydroxide and dilute/AR hydrochloric acid and transfer it to a 250 ml separating funnel. Add 25 ml. of a solution of 2'-2' biquinoline (100 mg. in 500-ml. amyl alcohol), shake vigorously and discard the aqueous layer. Run the organic layer into the cell of a spectrophotometer. Measure the absorbance against a reagent blank at 545 nm.

Compute the copper percentage by reference to the graph prepared with standard copper solutions.

Determination of small amounts of P_2O_5 in silica sand, carbonate rock (Spectrophotometry)

Reagents

1. **Vanadate reagent** – Dissolve 2.5 gm of ammonium vanadate in boiling water and cool the solution. Add 20-ml. conc. nitric acid, cool and dilute to one litre.
2. **Molybdate reagent** – Dissolve 50 gm. ammonium molybdate in hot water and dilute to 1000 ml.
3. **Standard P_2O_5 solution** – Dry potassium dihydrogen phosphate KH_2PO_4 at 110°C. Weigh 0.9588 gm. and dissolve in water. Add 5-ml. nitric acid and dilute to 500 ml.

Method

Take 0.1 gm. of finely pulverized sample in a beaker and add 5-ml. conc. nitric acid and a few drops of HF. Slowly evaporate over a hot plate, then dry and dehydrate. Add 5-ml. conc. nitric acid and 50-ml. water, boil and filter through No.40 Whatman filter paper. Wash the residue with hot water. Take the filtrate in a 100 ml. volumetric flask and make up the volume and mix thoroughly.

Take 5 ml. of the solution by pipette from the flask into a 100 ml. volumetric flask and add 10 ml. colourless nitric acid (1:1), 10 ml. ammonium vanadate solution and 10 ml. ammonium molybdate solution make the volume up to the mark with water and mix thoroughly. After 30 minutes, measure the absorbance at 400 nm. Take a reagent blank. Compute the percentage of P_2O_5 with Reference to the standard graph prepared using standard solutions containing 0.5, 1.0, 1.5, 2.0 and 2.5 mg per 100 ml. of P_2O_5 exactly in the manner stated above.

1.2.2.4 Determination of Water of Crystallization in Minerals (H_2O^+)

Direct determination (Penfield's method)

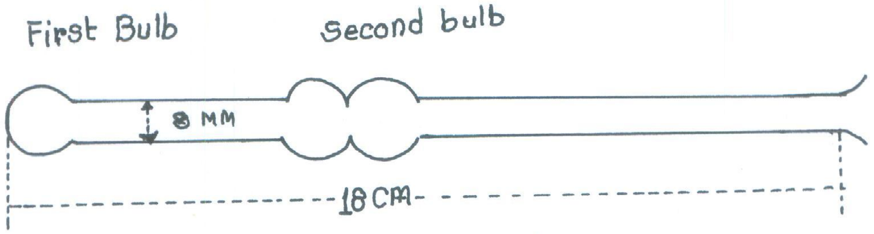
Dry the sample at 110°C for one hour. Take a dry penified tube and weigh. Pour in the lower bulb about 1 gm. of the sample through a capillary funnel. Take the weight of the tube again. The difference in weight will give the weight of the sample taken.

Place a moistened filter paper or cloth, around the second bulbs to ensure condensation of all water. Hold the tube horizontally, heat the first bulb on flame to red hot. Finally pull of the heated bulb along with the residue and cut it off with a flame from the rest of the tubed and seal off the cut end of the tube. Cool the tube, clean the external portion and take weight (W_1). Place the tube inside an electric oven at 100°C for 15 minutes. Remove the tube from the oven, cool in a desiccators and weigh W_2. The difference in weight will give the water.

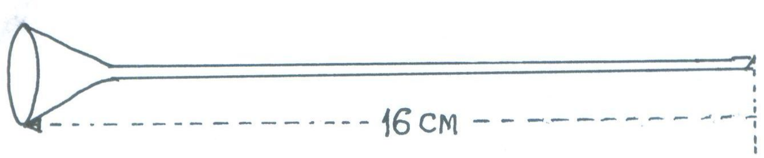
$$\% H_2O+ \quad = \quad \frac{(W_1 - W_2) \times 100}{\text{Weight of the sample taken}}$$

Note:

1. Water crystallization is combined water in the structure of the mineral. For example, in goethite ($Fe_2O_3.H_2O$), the water is inside the crystal structure, which is normally reported as H_2O+. Where the water is due to absorption in the form of moisture it is indicated as H_2O^-.
2. This method is suitable for minerals easily deprived of their water.
3. The minerals that do not give up their water wholly are talc,topaz, etc. and special methods are to be applied for them.
4. The Penfields tube for water determination in minerals is available in various forms.



Penfield's tube



capillary Funnel

1.2.2.5 Sulphur

The methods given below are applicable for the determination of sulphur in sulphide ores and materials high in sulphur.

Determination of sulphur in ores (Gravimetry)

A. Wet oxidization method

Principle

The finely ground sample is oxidized by means of a mixture of bromine and potassium bromate followed by nitric acid. The nitric acid is expelled by evaporation to dryness, followed by a second evaporation with hydro-chloric acid, which dehydrates the silica. Iron is now reduced to the ferrous condition and the silica and un-dissolved residue are filtered off. Sulphur is precipitated in a large volume of cold solution by barium chloride solution as $BaSO_4$, which is ignited and weighed.

Reagents

1. **Bromine-potassium bromide solution**: 320 gm of potassium bromide is dissolved in just sufficient water and 200 ml. bromine added. After mixing well, the solution is diluted to 2000 ml.
2. **Carbon tetrachloride saturated with bromine**.
3. **Barium chloride** – 10% solution

Procedure

The sample is ground to pass 80 mesh sieve. Take 0.1 gm of sample in a 250 ml. beaker and add 10 ml bromine – potassium bromide mixture for pyrrhotite ore or bromine carbontetrachloride reagent for pyrite ores. Cover the beakers and keep in a fume chamber (caution – bromine should be handled carefully and should not be inhaled, protective glass for eyes should be worn). The beaker should be shaken occasionally. After one hour, 15 ml conc. nitric acid is added and the mixture allowed to stand at room temperature overnight. The beakers are kept over a steam bath and allowed to dry. Ten ml. of conc. hydrochloric acid is now added and the solution again evaporated to dryness to expel all nitric acid. Silica is dehydrated by heating in an air-oven at $100^{o}C$ for one hour.

The beakers are removed and when cool, 5-ml. conc. hydrochloric acid and nearly 100-ml. water are added and boiled. After cooling, approximately 0.2 gm. of aluminium powder is added to the solution and stirred. When the iron has been reduced, the solution becomes colourless. The solution is filtered through No.40 Whatman filter paper into a 600-ml. beaker (preferably one litre beaker). The residue on the filter paper is washed 5 or 6 times with hot water. The solution in the large beaker is diluted to 500 ml. with cold water and 6 ml. (1:1) HCl added and mixed by stirring. Twenty ml. of 10% solution of barium chloride is now added. The solution is mixed by stirring. The $BaSO_4$ precipitate is allowed to settle overnight.

The clear solution is filtered through No.42 Whatman filter paper (or a filter crucible using suction).The precipitate is washed with cold water 10 times to remove the chloride ions.

Take the precipitate along with the filter paper in a weighed platinum crucible and slowly ignite at 950 to $1000^{o}C$ for one hour, remove and cool in a desiccator and weigh again. From the weight of the $BaSO_4$, calculate the percentage of sulphur.

$$S\,\% = \frac{\text{Weight of the } BaSO_4 \times 0.1374 \times 100}{\text{Weight of the sample taken}}$$

B. Fusion Method

Weigh 0.1 to 0.2 gm of sample, depending on whether the sulphur content is high or low, in a nickel crucible. Add about 2 gm of sodium peroxide and mix with a thin dry glass rod. Cover the mixture with a thin layer of the peroxide and then heat gently over a low flame at a temperature just sufficient to produce complete fusion. Do not hasten, a slow, gradual fusion is more successful as it will avoid loss due to spattering or burning of a hole in the crucible itself. The maximum temperature required is dull redness only. To obtain the liquid condition, 10 to 15 minutes heating would suffice.

Keep the melt over the flame for 5 minutes, and with the aid of tongs give the crucible a swirling motion 2 or 3 times during that period.

Remove from heat and allow it to cool in air slowly, (do not try to cool in water, it will cause an explosion), with the aid of a glass rod. Place the crucible in a 500 ml beaker and pour 100 ml water. Cover quickly with a watch glass to prevent loss by spattering. Remove and wash the crucible with water, policing it out. Boil for a few minutes with constant stirring to destroy excess of peroxide. If the supernatant liquid is greenish, it indicates manganese, add 2 to 5 ml. methyl alcohol and boil to precipitate manganese as MnO_2 and allow it to settle. The solution now will be clear.

Filter hot through Whatman No.40 filter paper in a 500 ml beaker (a bigger size filter paper is preferable) using funnel of large size so that the layer of precipitate on the filter paper will not be too thick. This will ensure quick filtering and efficient washing. Wash the residue with hot water 6 to 8 times. Discard the precipitate. The total filtrate and washings should have a volume of 250 to 300 ml. Add a few drops of methyl red and make slightly acidic with HCl (about 3 ml in excess). Heat to boiling and add slowly and with constant stirring 10 – 20 ml of 10% $BaCl_2$ solution. Keep it hot for a few minutes. Then remove from the flame and keep overnight to allow the precipitate to settle.

Filter through No.42 Whatman filter paper and wash the precipitate 8 to 10 times with hot water.

Transfer the residue along with the filter paper in a weighed platinum crucible and ignite the residue carefully at a temperature of $1000^{o}C$. Cool in a desiccator and weigh again. From the weight of the $BaSO_4$, calculate the percentage of S in the sample as follows:

$$S\ \% = \frac{\text{Weight of the } BaSO_4 \text{ x } 0.1374 \text{ x } 100}{\text{Weight of the sample taken}}$$

Determination of carbon-di-oxide (Gravimetry)

Principle

A known amount of the sample is made to react with an acid and the liberated carbon dioxide freed from impurities is absorbed in previously weighed sode asbestos bulb and weighed. From the difference, the percentage of carbon dioxide is calculated.

Reagents

1. **Dilute hydrochloric acid** 1:1 V/V
2. **Concentrated sulphuric acid.**
3. **Ascarite – solid.**
4. **Magnesium perchlorate – solid.**
5. **Copper sulphate solution.**

Procedure

Weigh 0.5 gm. of the sample to the flask of the CO_2 apparatus and cover it with water. Insert the stopper carrying the separatory funnel and the condenser. Connect the latter with the absorption vessel. Pass air that is free from CO_2 through the system. Close the stopper cock in the separatory funnel and insert the weighed absorption bulb in the train and also put the guard tube. Half fill the separatory funnel with 1:1 hydrochloric acid. Open the stop-cock in the separatory funnel and run acid into the flask slowly. When effervescence diminishes, start a flow of water in the condenser and heat the flask slowly so as to secure steady but quiet ebullition. 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. Close the inlet and outlet tube and disconnect the weighed bulb. Cool in a desiccators and weigh. The ascarite absorbs the carbon dioxide and the drying agent takes up the water formed in the reaction.

Reaction involved

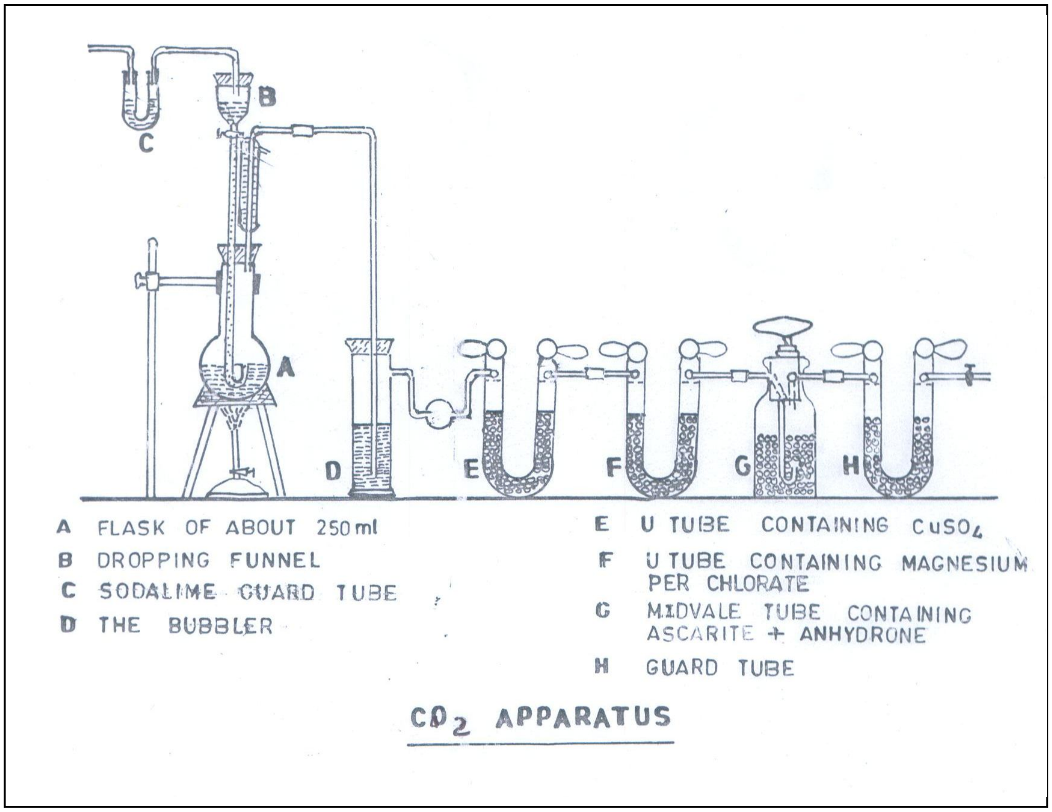
$$2\ NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$$

Calculation

$$CO_2\ \% = \frac{(A - B) \times 100}{C}$$

Where –

A = weight in gm. of the bulb after the test
B = weight in gm. of the bulb before the test
C = weight in gm. of the sample taken.



CO_2 APPARATUS

1.2.2.6 Determination of minute amount of Arsenic (Spectrophotometry heteropoly molybdenum blue method)

Principle

Following the separation of arsenic from matrix elements by distilledlation as the trichloride, the arsenic (III) is oxidized to the pentavalent state with nitric acid and ammonium molybdate is added to form a heteropolymolybdioarsenate which is then reduced by a suitable reducing agent to strongly coloured 'molybdenum blue' and measured at 840 nm.

Reagents

1. **Standard arsenic solution** – Dissolve 0.1320 gm. of Ar arsenic trioxide As_2O_3 in the minimum volume of 1 M sodium hydroxide solution, make slightly acidic with hydrochloric acid, make up to 100 ml in a volumetric flask.
   1 ml. = 1 mg. As
   A solution containing 0.001 mg. of As per ml. is prepared by dilution.
2. **Ammonium molybdate solution 0.1% W/V**, - Dissolve 5 gm. of ammonium molybdate $(NH_4)_6 Mo_7 O_{24}.4H_2O$ in approximately 200 ml. of 2.5 M sulphuric acid and dilute to 500 ml. with the same solution, store in a polythene bottle.
3. **Ascorbic acid solution**, 0.1% W/V – prepare fresh solution daily in water.
4. **Sulphuric acid 2.5 M** – Add 130 ml. of conc. sulphuric acid slowly while stirring to approximately 800 ml. of water. Allow the solution to cool to room

temperature, transfer to a 1 litre volumetric flask, and dilute to volume with water.

Procedure

Distill arsenic by the method given under arsenic ore and make up in a volumetric flask, to 250 ml. Take an aliquot of the distillate, add 10 ml. conc. nitric acid and evaporate to dryness, bake the residue at 130°C for 15 minutes to ensure complete removal of nitric acid. Cool and add 2 ml. ammonium molybdate, 2 ml. ascorbic acid solution, keep on a steam bath for 30 minutes. Transfer the solution in a 100 ml. volumetric flask and make it up to the volume with water and mix well. Determine the absorbance of the solution at 840 nm or with a red filter with maximum transmission above 700 nm. Prepare a standard curve from known amounts of arsenic treated in the same way as the unknown, carry out reagent blank, and measure the optical density against this. Compute the percent or arsenic from the standard graph.

Note

1. The acid concentration of the solution must be controlled. If the acidity is too low even molybdate alone will give a blue colour and if it is too high the colour due to arsenic is decreased in intensity.
2. Oxalic, tartaric, citric acids, fluorides and oxidizing agents interfere in this method.

Reference

E.B. Sandell – Colorimetric determination of traces of metals. Interscience publishers Inc., New York 1959, Page 279.

1.2.2.7 Determination of minute amount of Chromium (Spectrophotometry)

Diphenylcarbazide method

Principle

Hexavalent chromium reacts with 1-5-Diphenylcarbazide $CO(NH.NHC_6H_5)_2$ and produces a soluble violet compound in slightly acidic solutions (0.2 N). Measurement of the amount of reddish purple colour formed yields an estimation of chromium present (wave length 540 nm) or green filter may be used if a colorimeter is used.

Reagents

1. **1-5-diphenylcarbazide reagent 0.25%** - Dissolve 0.25 gm. $(C_6H_5NH.NH)_2CO$ in 100 ml. 95% ethyl alcohol or 50% acetone or isopropyl alcohol.
2. **Sulphuric acid 6N** – Add cautiously 167 ml. concentrated H_2SO_4 to distilled water and dilute to one liter.
3. **Standard Chromium Solution** – Dissolve 2.8283 gm. of pure $K_2Cr_2O_7$ in water and dilute to a liter in a volumetric flask. Pipette 20 ml. of this solution into a 2-liter volumetric flask and dilute to the mark with water.

   1 ml = 0.01 mg. Cr

Determination of Chromium (Minute Quantity)

Fuse 0.5 gm. of very finely ground rock powder with five times its weight of sodium peroxide in a nickel crucible (free from chromium and vanadium) and cool. Leach with hot water and filter through number 40 Whatman filter paper. Wash the residue with hot water. Add a few drops of alcohol and heat for about half an hour to destroy peroxide, manganate, if any, will be reduced. If any precipitate is there, filter through No.40 Whatman filter paper. Keep the solution to nearly 50 ml. If the solution is yellow in colour, it implies a higher percentage of Cr_2O_3. In such case, make up the solution in a volumetric flask and take an aliquot. If a very faint colour or no colour is visible, take the entire solution.

Neutralize the solution with dilute sulphuric acid. Add 2 ml 6 N H_2SO_4 more, add 2 ml of 0.25% diphenylcarbazide solution and make up to 100 ml. mix and obtain the optical density in a spectrophotometer at 540 nm or in a filter photometer using a green filter.

Compute the percent of Cr_2O_3 from a standard curve prepared under the same condition. Run a blank throughout the procedure.

Note :

1. If the ore contains vanadium, it should be separated by 8-hydroxyquinoline extract in chloroform as $V_2O_3\ (C_9H_6ON)_4$ complex at pH of about 4.
2. A suitable acidity for the chromium diphenylcarbazide reaction is 0.05-0.2 N.

1.2.2.8 Determination of Minute Amount of Iron (1:10 Phenanthroline Method)

Take 50 ml aliquot. Adjust the pH to 3.5 by sodium citrate solution. Add 1 ml of ascorbic acid solution. Stir the content thoroughly. Add 2 ml, 1:10 phenanthroline solution. Make up the volume to 100 ml in volumetric flask. Take a blank of all the reagents and make the volume to 100 ml. Measure the absorbance at 500 nm against the blank. Find corresponding amount of iron from the graph.

1	V_2O_5 (Spectrometically)	see Vanadium ores
2	Arsenic (Spectrometrically)	see Arsenic ores
3	Bismuth (Spectrometrically)	see Bismuth ores
4	Chromium	
5	Copper	
6	Cobalt (Spectrometrically)	see Cobalt ores
7	Nickel (Spectrometrically)	see Nickel ores
8	Tungsten (Spectrometrically)	see Tungsten ores
9	Molybdenum (Spectrometriclly)	see Molybdenum ores

ALUMINIUM ORES

Bauxite forms the main source of aluminium metal. It contains monohydrates aluminium oxides and trihydrate aluminium oxides in different proportions. It is associated with oxides and hydroxides of iron, titanium dioxide, silica, etc.

Bauxite is generally analysed for L.O.I., SiO_2 (total), SiO_2 (reactive), Al_2O_3, Fe_2O_3, TiO_2, CaO, MgO, P_2O_5 and V_2O_5 and Mn.

L.O.I. and Al_2O_3 are determined in separate portions of the sample. SiO_2, Fe_2O_3, TiO_2, CaO, MgO, P_2O_5 and V_2O_5 are determined after digestion of the sample and drawing aliquots from the main solution.

PREPARATION OF SAMPLE

Dry the well-ground sample (100 or 200 mesh) to constant weight at 140 + 2°C for one hour and use this for subsequent determination.

Determination of silica (Gravimetry)

Procedure

Take 1 gm. of dried bauxite sample in a 250 ml. beaker. Add 15 to 20 ml. conc. hydrochloric acid, 1 ml. conc. nitric acid and digest over a hot plate. After some time, add 5 ml. of 1:1 sulphuric acid, dry and fume off strongly. Moisten the dry residue with 1:1 sulphuric acid and add nearly 100 ml. of water and boil to dissolve the soluble salt. Filter the hot solution through What man filter paper No.40. Wash the residue 5 or 6 times with hot water.

Reserve the filtrate to prepare the main solution and determine the associated radicals.

Take the residue along with the filter paper in a platinum crucible and burn off the filter paper and ignite the residue. Cool in a desiccators and weigh. Moisten the residue with a few drops of 1:1 sulphuric acid and add 10-to 15-ml. hydrofluoric acid and keep over a hot plate or over a flame placing an asbestos board over it. Slowly evaporate and finally dry and ignite the residue, cool in desiccators and weigh. The difference between the two weights will give the silica content. Calculate the silica percentage as follows:

$$SiO_2 \text{ percentage} = \frac{(W_1 - W_2) \times 100}{W_3}$$

Where –

W_1 is the weight of the crucible + material after ignition.

W_2 is the weight of the platinum crucible + material after hydrofluorization and

W_3 is the weight of the sample taken.

Preparation of the main solution

Fuse the residue after hydrofluorization with 0.5 gm. potassium pyrosulphate and extract the mass in the preserved filtrate by boiling. Cool the solution.

Transfer the solution into a 250 ml. volumetric flask, make up to the mark and mix the contents well. Treat this as the main solution. An aliquot is taken for the determination of Fe_2O_3, TiO_2, P_2O_5, V_2O_5, CaO, MgO, etc. Follow the procedure given in chapter on determination of Major and Minor Elements from the Stock Solution.

Determination of reactive silica (Gravimetry)

Outline of the method

The sample is dissolved in mixture of acids (HCl, HNO_3 H_2SO_4) and evaporated to fumes. HF is added and the solution filtered. The residue is hydrofluorized. The loss in weight of the residue represents non-reactive silica.

Reactive silica is obtained by deducting the percentage of non-reactive silica from the percentage of total silica.

Procedure

Transfer 1 gm. of sample into a beaker. Add 25-ml. conc. hydrochloric acid and 5-ml. conc. nitric acid and keep over a hot plate. After sometime, add 20-ml. 1:1 sulphuric acid. Heat slowly and continue heating until copious fumes are liberated and finally dry. Cool and add about 100-ml. water and few drops of 1:1 sulphuric acid and boil till a clear solution is obtained. Add 30 ml. 40% hydrofluoric acid from a polythene measuring cylinder, boil for one minute and filter at once through No.40 Whatman filter paper using a little pulp. Wash the residue with hot water 5 to 8 times.

Transfer the filter paper along with the residue into a platinum crucible, ignite it in a furnace at 900 to 1000°C for one hour, cool and weigh. Add 5 to 10 drops of 1:1 H_2SO_4 and half a crucible hydrofluoric acid and evaporate slowly to dryness. When dry, ignite over a flame. Cool in desiccators and reweigh.

$$\text{Non-reactive silica percentage} = \frac{A \times 100}{B}$$

Where –

A = loss of weight of the residue after HF, and
B = weight of the sample taken.
Reactive silica percentage = Total silica – Non-reactive silica

N.B.: From our experience, it is observed that this method gives a fair idea of reactive silica in routine analysis of bauxite. This is also corroborated by some of the Indian aluminium companies in their communications. For accurate determination of reactive silica, the bomb digestion method, specifying temperature and pressure is recommended**.**

ALUMINOSILICATES AND OTHER SILICATES

Some silicates are decomposed by strong mineral acid and the silica passes as insoluble residue. This is then dehydrated and separated by filtration. The silica is estimated from the insoluble residue by hydrofluorisation.

Many silicates are not completely decomposed by strong mineral acid or they are not at all affected by strong mineral acid (except hydrofluoric acid). Silica being acidic in nature fusion with alkali salt is most preferred to break a complex silicate. The choice of flux depends on the properties and presence of certain elements in the silicate. Anhydrous sodium carbonate is most commonly used to break complex silicate. Additions of potassium carbonate lower the fusion temperature and potassium carbonate being more alkaline in nature increase the activity of flux. Potassium carbonate is hygroscopic and more corrosive than anhydrous sodium carbonate care must be taken to avoid loss due to sputtering. A small piece of filter paper is added to molten mass to dissolve the more refractory silicates. Sodium carbonate with little borax or boric acid is used to dissolve some hard silicate and when the silicate or the sample contains fluorine. Excess of borate must be removed before estimation of silica.

A. Estimation of silica (sodium carbonate fusion)

Mix thoroughly 4 to 6 g of anhydrous sodium carbonate with 1 g of rock or mineral powder in a platinum crucible of 20-30 ml capacity. Place the crucible, covered at first, over a moderately low flame, increase this gradually to a maximum (approximately 1000^{o}C) and maintain it there till the mass is quiescent. There should be no violent action. Cool the crucible. Place the crucible in 250 ml beaker in horizontal position. Cover the crucible completely with demineralised water. Now add 10-15 ml concentrated hydrochloric acid. Cover the beaker with watch glass. Allow the reaction to complete. Now heat the beaker on low flame. Remove the crucible. Now transfer the beaker to hot plate. Allow all solvent to evaporate. Near completion the mass should be occasionally stirred to avoid formation of lumps. After evaporation of all solvent break any lump thus formed. Bake the mass at 110^{o}C for 1 hour. Remove the beaker from the hot plate. Cool the beaker. Moisten the mass with 1-2 ml concentrated hydrochloric acid and add 50 ml demineralised water. Boil this on burner. Cool this and filter through Whatman 40. Wash the residue 5-6 times with hot water transfer all silica residue from the beaker with policeman or a small piece of filter paper. Preserve the filtrate for estimation of other radicals. Transfer the filter paper into a platinum crucible. Ignite this 1000^{o}C. Cool the mass in desiccator and weigh. Moisten the mass with DM water. Add 2-3 drops of dil sulphuric acid. Add 10-15 ml 48% hydrofluoric acid. Place the crucible on asbestos sheet on a low flame or on a low temperature hot plate. Expel all acid from the crucible. Now heat the crucible on a low flame initially and finally to a blast flame (1000^{o}C) for about 5 minutes. Cool the crucible in desiccater. Weigh the mass. The loss in weight will be silica. Fuse the residue after silica determination with little potassium pyrosulphate. Extract the mass in preserved filtrate. Cool the filtrate and make up to 250 ml.

B. Estimation of silica (when the sample contains fluorine) – Borate fusion:

Mix thoroughly 4-6 g of anhydrous sodium carbonate & 0.5 g Borax with 1 g of fine powdered rock or mineral in a 20-30 ml platinum crucible. Place the crucible, covered at first, over a moderately low flame, increase this gradually to a maximum (approximately 1000^{o}C) and maintain it there till the mass is quiescent. There should be no violent action. Cool the crucible. Place the crucible in 250 ml beaker in horizontal position. Cover the crucible completely with demineralised water. Add

10-15 ml concentrated hydrochloric acid. Cover the beaker with watch glass. Allow the reaction to cease. Wash the watch glass in to the beaker. Now slowly heat the content on low flame to remove all mass from the crucible. Remove the crucible and wash it thoroughly.

(**Removal of excess borate**) – Transfer the contents of the beaker completely into 15-20 cm diameter china clay dish. Evaporate the contents carefully on a low flame. Expel all liquid from the dish. Remove the dish from the flame. Add 4-5 drops of dilute sulphuric acid. Add 10 ml methanol. Ignite the methanol with open flame. Stir the mass. Apple green flame will indicate the presence of borate in the mass. Cool the dish. Again repeat the process of removal of borate by additional quantity of sulphuric acid and methanol till all borate is burnt**.**

Cool the masses add 5 ml concentrated hydrochloric acid and 50 ml demineralised water. Boil the content on burner. Cool and filter through Whatman 40. Wash the residue 5-6 times with hot water. Preserve the filtrate for estimation of other radicals. Transfer the filter paper into a platinum crucible. Ignite this at 1000^{o}C in muffle furnace. Cool the mass in a desiccator and weigh. Moisten the mass with little DM water. Add 2-3 drops dilute sulphuric acid. Add 10-15 ml 48% hydrofluoric acid to the mass. Place the crucible on asbestos sheet on a low flame or on a low temperature hot plate. Expel all acid from the crucible. Now heat the crucible initially on a low flame and finally to a blast flame (1000^{o}C) for about 5 minutes. Cool the crucible in desiccator. Weigh the mass. The loss in weight will be the quantity of silica. Fuse the residue in the crucible with little potassium pyrosulphate. Extract the mass in the preserved solution. Cool the filtrate and make up to 250 ml.

Determination of Fe_2O_3, CaO, MgO, Al_2O_3, TiO_2 etc.: Follow the procedure given under the chapter on determination of major and minor constituent from the stock solution.

Determination of Loss on Ignition (L.O.I.)

Loss on Ignition: Weight 1 g of dry sample in silica or platinum crucible. Place this crucible in muffle furnace at a temperature below 300^{o}C. Raise the temperature of the furnace to 1000^{O}C. Keep this at this temperature for about 30 minutes. Cool the crucible in desicater. Weigh the crucible. Find the loss in weight.

$$\%\ \text{Loss on Ignition (LOI)} = \frac{\text{Loss in weight x 100}}{\text{Weight of the sample}}$$

ANTIMONY ORES

The important antimony-bearing mineral is stibnite (Sb_2S_3), which is the main commercial source of antimony. A relatively large amount of antimony is present in the sulphide ores in the form of tetrahedrite (sulphide of Sb), bournonite (sulphide of Cu, Pb and Sb), etc.

Determination of antimony

Procedure

Take 0.5 to 1 gm of finely powdered ore in a 50 pyrex or corning conical flask. Add 3 to 5 gm. potassium sulphate and 15 ml. conc. sulphuric acid and a piece of paper to reduce the antimonic compound. Put a clean funnel over the flask and heat the mixture gradually at low temperature and then with a full flame. Heating is continued till carbon is completely oxidized, most of the free acid is driven off and a clear solution is obtained (taking care not to expel all the H_2SO_4). The melt is allowed to cool over the sides of the flask by rotating gently during cool.

Add 50 ml 1:1 hydrochloric acid and dissolve the melt by gentle warming. Transfer the contents of the flask to 500-ml. beakers, rinse the original flask with 25 ml. conc. hydrochloric acid. Pass a rapid current of H_2S through strong acidic solution to precipitate arsenic sulphide through a double filter paper moistened with (2:1) HCl, the beaker with (2:1) HCl. Wash the precipitate 5 or 6 times with this acid. Antimony passes into the filtrate together with the other elements present in the ore.

Dilute the filtrate with three times of its volume of warm water and then saturate with H_2S gas. Antimony sulphide together with the other elements of the hydrogen sulphide group will precipitate. Filter through no.40 Whatman filter paper and wash the residue with dilute sulphuric acid (1+1) saturated with hydrogen sulphide till free from chloride ions. Reject the filtrte. Treat the precipitate in the filter paper with 10 to 20 ml. mixture of AR quality sodium sulphide and sodium hydroxide (70 gm. of Na_2S with 40% of NaOH diluted to 1000 ml.). This operation will separate antimony sulphide from the sulphide of Cu, Pb, Cd, Bi, etc.

Take the filtrate and the washings containing antimony, add 2 g of potassium sulphate and 10 ml. conc. sulphuric acid and heat until sulphur is destroyed and most of the free acid has been expelled. Dissolve the melt in hydrochloric acid and titrate with 0.1 N potassium permanganate.

The titration is ordinarily carried out in a solution of trivalent antimony, which contains both sulphuric and hydrochloric acids. In a volume of 200 ml. there should be progressively less hydrochloric acid. Add hydrochloric acid approximately in the following proportion to the solution.

10 ml. H_2SO_4 ..	30 to 35 ml. HCl
20 ml. H_2SO_4 …	15 to 30 ml. HCl

Dilute to 200 ml. with water, and cool to 10 – 20°C, then titrate with standard permanganate solution until a decided pink colour persists for 10 to 30 seconds.

Calculate the percent of antimony from the following factor:

1 ml. of 1 N $KMnO_4$ = 0.06057 g. of Sb.

ARSENIC ORES

The principal minerals are arsenopyrite (FeAsS), realgar (As_2S_2) and orpiment (As_2S_3) and many arsenides and sulpharsenides of lead, copper, gold and tin.

Determination of arsenic (Volumetry)

Principle of the method

Arsenic is distilled out at 110°C in the presence of cuprous chloride and hydrochloric acid as arsenious trichloride ($AsCl_3$). The distillate is trapped in water and determined volumetrically by titrating with standard iodine solution at a specified pH.

Procedure (for sulphide minerals)

Weigh 0.5 to 5 g (according to the anticipated amount) of the finely powdered sample; add 15 ml of fuming nitric acid and digest over hot plate at low temperature. Add 10 ml 1:1 sulphuric acid and evaporate to dense fumes.

Allow the mass to cool. Add water and transfer the entire mass into a distillation flask. Wash the beaker thoroughly and pour the washings into the distillation flask. Add 1 gm of hydrazine sulphate, 0.5 g of cuprous chloride to ensure reduction of arsenic to the trivalent condition.

Add 70-ml. conc. arsenic free hydrochloric acid, and set up the distillation apparatus. The end of the condenser should be submerged in 50 ml. of water in the collecting beaker. Slowly raise the temperature and distilled out nearly 100 ml. between 100 and 110°C (at a very slow rate). The collecting beaker can be graduated to indicate the various volumes of the distillate. Disconnect, wash out the condenser into the collecting beaker. Transfer the distillate to a 500 ml. beaker for titration. Cool, add a piece of litmus paper and make it slightly alkaline with 20% NaOH, then re-acidify slightly with HCl. Cool again. To the cold, slightly acidic solution, add 3-4 g. of $NaHCO_3$ (in excess), and then a little starch solution. Titrate with standard iodine solution to permanent blue tinge.

Calculate the percentage of the arsenic in the sample using the following factor:

1 ml. 1N iodine = 0.03746 gm. of As
= 0.04946 gm. of As_2O_3

Reaction involved:

$$H_3AsO_3 + I_2 + H_2O = H_3AsO_4 + 2HI$$

BARIUM ORES

The chief minerals of barium are barite ($BaSO_4$) and witherite ($BaCO_3$).

Barite is generally analysed for matters soluble in water, $BaSO_4$, SO_3, Fe_2O_3 and Al_2O_3 (combined), CaO, MgO, VM at $98^o – 102^oC$**.**

Determination of matter soluble in water

Procedure

Weigh 10 g of the finely powdered materials in 500 ml. beaker, add about 150 ml. of freshly boiled neutral water (pH-7), boil for about 10 minutes, cool the mixture to room temperature. Make up to 250 ml. with freshly boiled and cooled neutral water in a volumetric flask. Shake and filter through a dry funnel using No.40 Whatman filter paper in a beaker. Take 100 ml. of the filtered solution in a weighed platinum dish and slowly evaporate to dryness on a water bath. Dry the residue at a constant weight in an oven at 105 to 110^oC. Cool in a desiccator and weigh. Difference in weight gives residue in 100 ml. of the solution. Compute the result as follows:

$$\text{Matter soluble in water \%} = \frac{W_2 \times 2.5 \times 100}{W_1}$$

Where- W_2 is the weight of the residue in the platinum dish.
W_1 is the weight in gram of the material taken.

Note: Test the water-soluble extract with a pH meter and report the acidity or alkalinity, if any, calculates as H_2SO_4 or Na_2CO_3.

Determination of barium sulphate ($BaSO_4$) (Gravimetry)

Principle

The sample is fused with a mixture of sodium and potassium carbonate, leached with water to remove silica or other soluble sodium compounds. Barium remains insoluble as carbonate together with other heavy metals. The residue is washed with sodium carbonate solution to remove the adhering sulphate. The insoluble carbonates are dissolved in hydrochloric acid. The R_2O_3 groups are separated and filtered. The filtrate is acidified with hydrochloric acid and barium is precipitated from the acidic solution as barium sulphate with the addition of ammonium sulphate that is ignited and weighed.

Procedure

Weigh 0.2 g. of finely ground sample in a platinum crucible and add 1.5 g. of Na_2CO_3 and 1 g. of K_2CO_3 cover and fuse the mixture over a high temperature burner or in a furnace at 1000^oC for about 30 minutes. Take the crucible out of the hot zone and rotate it so that the fusion will solidify in a thin layer by the side of the crucible. This will shorten the time required for leaching. When cool, leach out the fusion with 200 ml. boiling water in a 500-ml. beaker. Filter through No.40 Whatman filter paper and wash the filter paper and residue 10 to 12 times with hot sodium carbonate solution and finally with hot water till free from sulphate. (Test the filtrate with $BaCl_2$ solution). Preserve the filtrate for the determination of SO_3.

Dissolve the residue from the filter paper and a small portion of the solid adhering to the platinum crucible with hot 1:1 hydrochloric acid. Add 1 g ammonium chloride and neutralize with NH_4OH using methyl red as Indicator. Boil and filter through No.41 Whatman filter paper, wash the residue 4 or 5 times with hot water. Preserve the filtrate. Dissolve the residue in hot hydrochloric acid and reprecipitate with NH_4OH as before. Wash the residue with hot water 5 to 6 times. This operation will bring out any barium that might have been occluded in the R_2O_3 precipitate. Mix both the filtrates and proceed.

Take the filtrate in a 500 ml. beaker. Add a few drops of methyl red indicator and neutralize the solution with hydrochloric acid and add 2 ml. more conc. hydrochloric acid. Dilute to 400 ml. with distill water, bring the solution to boil and add 20 ml. 10% hot ammonium sulphate solution drop wise with constant stirring, boil for five minutes, remove from the flame and allow it to stand for a at least 4 hours or preferably overnight. Filter through No.42 Whatman filter paper and wash the residue thoroughly with warm water containing five drops sulphuric acid per liter and then with cold water until filtrate is free from chloride ions. Transfer the residue along with the filter paper in a weighed platinum crucible, slowly burn off the filter paper and ignite the residue at 850°C to 900°C for 30 minutes. Cool in desiccators and weigh. Calculate the percentage of $BaSO_4$ as follows:

$$BaSO_4\,\% = \frac{(A-B) \times 100}{C}$$

Where - A = weight of the platinum crucible and the ignited Barium sulphate,

B = weight of the empty platinum crucible

C = weight of the sample taken.

Notes :

1. Fusion is started with a low flame, which is gradually raised to the full blast. This precaution is necessaryto prevent loss by overflowing.
2. To shorten the time for leaching, the melt in the platinum crucible should be solidified by the side of thecrucible as a thin layer.
3. If the barite contains small amount of iron, the removal of R_2O_3 group is not necessary as there will be little co precipitation and this step may be emitted. The residue on the filter paper after removal of the sulphate ions may be dissolved in hot hydrochloric acid and directly proceed for the precipitation of $BaSO_4$.
4. Solubility of barium sulphate increases in hot water or in dilute hydrochloric or nitric acid. Hence, the precipitation must be made in solution that contains preferably not over 1% of the mineral acid.
5. Thewashing of the precipitate should not be excessive. In accurate analysis, the washing should not be carried out beyond the point at which 20 ml. of the washings give but a faint opalescence with silver nitrate.
6. Filter paper containing the precipitate of $BaSO_4$ should be burnt below 600°C. At higher temperature carbon in the paper reduces barium sulphate to barium sulphite. To ensure complete conversion to $BaSO_4$. Remove the crucible after burning of the paper and add 2-3 drops of nitric acid and 2-3 drops of dil sulphuric acid and ignite the ppt
7. .Ignition should be done at approximately 900°C although the precipitate suffers no appreciable dissociation at temperature up to 1400°C.
8. If the analysis is a continuing one, ignite the filter paper along with the NH_4OH precipitate in a weighed platinum crucible and weigh. Report this as mixed oxide percent.

9. The method given here for $BaSO_4$ determination is for barite sample containing all the barium as $BaSO_4$ only. If mineralogical studies indicate the presence of other minerals of barium, then barium from hydrochloric acid leaching should be determined and deducted from the barium reported as $BaSO_4$.

Determination of SO_3

Take the filtrate reserved for the determination of SO_3, add few drops of methyl red indicator and acidify with HCl, make the volume to nearly 300 ml. with water, and adjust the acidity such that each 100 ml. of solution contain nearly 1 ml. of HCl. Boil and add 20 ml. of 10% $BaCl_2$ solution drop wise with constant stirring, boil and allow to settle at least for four hours or preferably overnight. Filter through No.42 Whatman filter paper and wash the residue five to six times with hot water only till free from chloride ions. Wrap the precipitate in the paper, place it in a weighed platinum crucible, dry, char and ignite at 900^oC for 30 minutes. Cool in a desiccators and weigh. Calculate the percentage of SO_3 as follows :

$$SO_3 = \frac{(A-B) \times 0.3430 \times 100}{C}$$

Where - A = Weight in g. of the platinum crucible And ignited residue
B = weight in g. of the empty platinum crucible,
C = weight in g. of the sample taken.

Determination of silica (Gravimetry)

Principle

The material is fused with a mixture of sodium carbonate and potassium carbonate and leached out with hot water and filtered. Silica is recovered from the residue as well as from the filtrate and the silica is determined by dehydration and hydrofluorization.

Procedure

Take 0.5 to 1 g. of the finely pulverized sample in a platinum crucible, add about 3 grams of AR sodium carbonate and about 1 gm. of AR potassium carbonate, mix with a dry glass rod and fuse in a muffle furnace or over a burner. Take the crucible out of the hot zone and rotate it so that the fusion will solidify in a thin layer by the side of the crucible. Cool the melt. Leach out the fusion with 200 ml. of water by boiling over a flame.

Filter the solution through Whatman filter paper No.40 and wash the residue ten times with a hot solution of sodium carbonate till free from sulphate ions (Test the filtrate with $BaCl_2$ solution). Proceed with the filtrate (a) and residue (b) as follows: -

1. Acidify the filtrate (a) with conc. hydrochloric acid, evaporate, dry and bake the solid material at 115 – 120^oC for half an hour. Add 10 ml. of dil. hydrochloric acid and about 50 ml. of water, boil and filter through No.40 Whatman filter paper. Wash the residue with hot 1% hydrochloric acid and finally 5 times with hot water. Preserve the residue (A) in filter paper and the filtrate (A).

2. Dissolve the residue (b) in hot hydrochloric acid, also wash the platinum crucible in which fusion was carried out with hydrochloric acid to remove the adhering particles. Evaporate, dry and bake. Add 5 ml. of conc. hydrochloric acid and about 50 ml. of water boil and filter through No.40 Whatman filter paper. Wash the residue with hot 1% hydrochloric acid and finally with hot water. Preserve the residue (B) in the filter paper and the filtrate (B).

Take the residue A and B along with the filter paper in a platinum crucible and slowly burns off the filter paper and ignite the residue. Cool in a desiccators and weigh. Add few drops of 1:1 sulphuric acid and about 15 ml. of hydrofluoric acid evaporate to dryness, ignite and weigh.

Calculation SiO_2 % $= \frac{(A-B) \times 100}{C}$

Where - A = weight of the crucible along with Residue before treatment with hydrofluoric acid,

B = weight of the crucible with material After treatment with Hydrofluoric acid.

C = weight in gm. of the material taken.

Determination of mixed oxides (Gravimetry)

Principle

From the combined filtrate obtained from the determination of silica, Ba is removed; iron and aluminium hydroxides are precipitated with ammonium hydroxide. The precipitate is ignited and weighed as oxides of iron and alumina.

Procedure

Mix the filtrate A and filtrate B of the above operation (i.e. filtrate of SiO_2 determination), also fuse the small amount of material adhering to the platinum crucible after hydrofluorization of silica with small amount of potassium pyrosulphate, take up the hydrochloric acid and mix with the same solution. Evaporate to reduce the volume of the solution. Adjust the acidity of the solution s given earlier for $BaSO_4$ precipitation. Add 2 ml. 10% ammonium sulphate solution and boil and allow the residue to settle for at least two hours. Ammonium sulphate solution is added to ensure complete precipitation of barium. Filter through No.42 Whatman filter paper; wash the residue with hot water 5 to 6 times. Discard the residue ($BaSO_4$).

Take the filtrate, add 2 g. of ammonium chloride and precipitate iron and aluminium with ammonium hydroxide, boil and filter through No.41 Whatman filter paper. Wash the residue with hot 1 % ammonium nitrate solution till free from chloride ions. Preserve the filtrate for the determination of CaO and MgO. Ignite the precipitate in a weighed platinum crucible at 1000^{o}C, cool in desiccator and weigh. Compute the percent of combined iron and aluminium oxide as follows:

$$\text{Iron and aluminium oxides \%} = \frac{A \times 100}{W}$$

Where - A = weight of the mixed oxide.
W = weight of the material taken.

Note: If the sample contains phosphorus and titanium, the same will also be precipitated along with the ammonia precipitate.

Determination of CaO and MgO (EDTA Complexometry)

Follow the procedure given in chapter on analysis of major and minor elements from the stock solution.

Determination of barite in Cu-Pb-Zn ores

Some complex Clu-Pb-Zn ores of India contain barite as their associated mineral. In such case, follow the following procedure for the determination of $BaSO_4$.

Procedure

Take 0.5 to 1 g. of the material according to the anticipated amount of the $BaSO_4$ in a beaker; add 10 ml. of conc. hydrochloric acid and 5 ml. of conc. nitric acid digest over a hot plate. After sometime, add 5-ml. 1:1 sulphuric acid and fume up cool and add 10 ml of dilute sulphuric acid and about 150 ml. of water boil and filter through no.40 Whatman filter paper. Wash the residue with hot water. In this operation, lead will come as lead sulphate along with the barite as residue in the filter paper. Take the filter paper along with the residue in a beaker; add 50 ml. of a mixture of acetic acid and ammonium acetate solution and boil. Filter through No.40 Whatman filter paper; wash the residue 5 to 8 times with hot water.

Take the filter paper along with the residue in a weighed platinum crucible, burn off the filter paper and ignite the residue, add few drops of the sulphuric acid and about 15 to 20 ml. of hydrofluoric acid and evaporate slowly till finally dry and ignite at a low heat.

Fuse the remaining residue in the platinum crucible with about 0.5 gm. of potassium pyrosulphate. Take up the fused material with sulphuric acid and water. Adjust the acidity of the solution such that every 100 ml. contain 1 ml. of acid. Make up the volume to nearly 400-ml. boil and allow to settle for at least four hours preferably overnight. Filter through No.42 Whatman filter paper. Wash the residue with water till free from chloride ions. Take the residue along the filter paper in a weighed platinum crucible, burn off the filter paper and finally ignite the residue. Cool in a desiccators and weigh. Difference in weight will give $BaSO_4$. Compute % of $BaSO_4$ as follows:

$$BaSO_4\ \% = \frac{(A-B) \times 100}{C}$$

Where - A = weight of the platinum crucible and the Barium sulphate.
B = weight of the empty platinum crucible.
C = weight of the sample taken.

Note:

1. Potassium pyrosulphate fusion will help in decomposing any unattached material and also will supply sulphate ions for $BaSO_4$ precipitation.
2. It is observed that after hydrofluorization some iron remains in the residue. Fusion and precipitation of $BaSO_4$ in a large volume will eliminate contamination of iron with $BaSO_4$.

Determination of matter volatile at 98°C

Procedure

Heat a clean empty vitrosil or platinum crucible and lid in the oven at 98°C to 102°C for half an hour. Remove the crucible and the lid from the oven and cool in a desiccator for 10 minutes. Weigh the empty crucible and lid and introduce about 1 g of the sample. Weigh the crucible and its contents to determine the weight of the sample. Tap the crucible on a clean hard surface until the content forms an even layer at the bottom of the crucible. Maintain the oven at a steady temperature of 102°C. Place the covered crucible containing the barite in the oven and heat for a period of 15 minutes. Remove, cool in a desiccators and weigh the crucible. Calculate the loss in weight. Compute as follows:

$$\text{VM \%} = \frac{W_1 \times 100}{W_2}$$

Where - W_1 = is the loss in weight of the material
W_2 = is the weight of the material taken

BISMUTH ORES

Bismuth is generally found as an associated element in polymetallic ores. It is specially determined in lead concentrates.

Determination of bismuth (Spectrophotometry)

Principle

Bismuth is determined by spectrophotometric measurement at 460 nm of the absorbance of the yellow iodobismuthite complex BiI_4 formed in a 0.5 M sulphuric acid – 0.12 M potassium iodide in a reducing medium of hypophosphorus acid.

Reagents

1. **Standard bismuth solution** – Dissolve 0.25 g. of pure bismuth metal by heating with 30 ml. 30% nitric acid. Boil the solution gently for 10 minutes, then cool, and dilute to 250 ml. with water.
   1 ml. = 1 mg. Bi

Dilute this solution to prepare -

1 ml.= 0.1 mg. of Bi

2. **Potassium iodide solution 10% /W/V**
3. **Sodium hypophosphite solution 30% W/V.**
4. **Sulphuric acid 50%** W/V.

Preparation of solution

Take 1 g. to 2 g. of finely pulverized ores according to the anticipated amount of bismuth in a 500 ml. beaker, add 15 ml of conc. hydrochloric acid and 10 ml. of fuming nitric acid and keep over a hot plate, when the brisk reaction subsides add 10 ml. of 1:1 sulphuric acid and fume off. Add 5-ml. 1:1 sulphuric acid and 100-ml. water, boil and filter through No.40 Whatman filter paper. Wash the residue with water 5 to 10 times. Discard the residue and proceed with the filtrate. Add 1 g. of ammonium carbonate to the filtrate, make it ammonical, boil and filter through No. 41 Whatman filter paper (this operation will remove copper). Wash the residue with ammonical hot water till the filtrate is free from the blue colour of ammonia-copper complex. Reject the filtrate. Dissolve the residue in hydrochloric acid. Warm the solution to 80^{o}C and pass H_2S gas for 30 minutes. Filter through No.40 Whatman filter paper. Wash the residue with 1% hydrochloric acid saturated with H_2S. Dissolve the residue in the filter paper in a minimum amount of nitric acid. If the amount of bismuth present is small, use the entire amount of the solution, otherwise make up the solution and proceed by taking an aliquot for the determination of bismuth.

Procedure

Take an aliquot or the entire solution if Bismuth presence is less in a 100 ml. volumetric flask. Add 3 ml. 50% sulphuric acid, 1 ml. 30% sodium hypophosphite solution and 10 ml. 10% potassium iodide solution, mix thoroughly, and allow the solution to stand for 10 minutes. Dilute to the required volume with water and mix. Take reagent blank along with the sample. Determine the absorbance of the solution at 460 nm against water as Reference solution. Correct the absorbance values obtained for the blank solution. Compute the percentage of bismuth from the standard calibration curve prepared from the standard solution.

Notes:

1. Hypophosphorus acid, which is produced by the reaction of the mineral acid with sodium hypophosphite, eliminates interference from free iodine during complex formation. This reduction prevents the air oxidation of iodide ion to iodine.
2. Lead is precipitated as sulphate and copper, iron etc. are removed.
3. As reduction with hypophosphorus acid is slow, a standing period of 15 minutes is recommended to ensure complete destruction of any free iodine that is formed by the reaction of iodide ions with the oxidizing sample constituent. Suspended matter, causing turbidity in the final solution, may be removed by centrifuging or filtering the solution before measuring the absorbance of the bismuth iodide complex.

4. The coloured product can be extracted with higher alcohols and esters. A mixture of amyl alcohol and ethyl acetate has been recommended for the purpose. Extraction enables bismuth to be determined in the presence of coloured ions such as nickel, cobalt and chromium.

References

1. E.B. Sandell – Colorimetric Determination of Traces of Metals, 3rd Edition, Interscience, New York, pp – 33 – 336 (1959).
2. W.F. Hillebrand, G.E.F. Laundell, H.A. Bright and J.I. Hoffman Applied Inorganic Analysis, 2nd Edition, John Wiley and Sons, Inc., New York, p – 232 (1953).

CHROME ORES

Chromite is the most important ore of chromium. It is a mineral of variable composition. Theoretically, its composition is FeO, Cr_2O_3, but in nature, there is considerable replacement of both Fe and Cr by other elements. Its formation may be represented as (Fe, Mg) O. (Cr, Al Fe)$_2$O$_3$.

The radicals normally determined are Cr_2O_3 (total), SiO_2, Al_2O_3, FeO, MgO, CaO, P and S.

Determination of Cr_2O_3 (Volumetry)

Principle

The sample is fused with sodium peroxide in a nickel crucible. The sodium chromate formed is leached out with water and the acidified solution is treated with known excess volume of ferrous ammonium sulphate. The excess of ferro-ammonium sulphate is estimated with standard potassium dichromate using barium diphyenylamine sulphonate as indicator. A blank is taken and the Cr_2O_3 is determined from the amount ferrous ammonium sulphate used up.

Reagent

$FeSO_4(NH_4)_2SO_4.6H_2O$ – (0.1N solution) : Dissolve 39.2 g. of the salt in 250 ml. of water, add few drops of sulphuric acid to clear up the solution. Make the volume one liter.

Procedure

Grind the ore in an agate mortar to the finest possible powder. Weigh 0.2 g. into a nickel crucible, add about 1 g. of sodium peroxide, mix thoroughly with a glass rod. Heat the crucible gently over a low flame until the mass melts. Keep fused for a further 10 minutes at a cherry red heat. Allow the crucible to cool and place it in a 500 ml. beaker containing little water, cover the beaker. Add nearly 100 ml. of water and after the violent action has subsided remove the crucible with a glass rod and wash it thoroughly, collecting the washing in the same beaker, boil and filter through No.40 Whatman filter paper. Wash the residue with hot water till free from chromate ions. As there are chances of some chromium being held up by the residue, dissolve the residue in the filter paper in minimum amount of hydrochloric acid, dilute, add sodium peroxide slowly with constant stirring till a permanent precipitate is obtained, boil and filter through No.40 Whatman filter paper. Wash the residue five to six times with hot water. Combine this filtrate with the previous filtrate. Boil for half an hour to decompose hydrogen peroxide. Cool, acidify with 1:1 H_2SO_4, add 5 ml. more, cool it and add a measured amount of ferrous ammonium sulphate solution in excess. The solution becomes green, add 5 ml. of orthophosphoric acid and titrate the excess of ferrous ammonium sulphate with 0.1 N potassium dichromate solution using barium diphenylamine sulphonate as indicator until the colour changes to violet.

. Run a blank for the amount of ferrous ammonium sulphate added and from this, determine the actual volume of the ferrous ammonium sulphate solution, which was oxidized by the dichromate originating from the chromite. Compute the percent of Cr_2O_3 from the following factor:

1 ml. 1 N $K_2Cr_2O_7$ = 0.02534 g. of Cr_2O_3

Note: The chromate solution is to be boiled for half an hour to remove the hydrogen peroxide before it is acidified. This is necessary because the hydrogen peroxide reduces chromium (VI) to the trivalent state in acid solution.

Reactions involved are:

1. $2FeCr_2O_4 + 7Na_2O_2$ --- $2NaFeO_2 + 4Na_2CrO_4 + 2Na_2O$
2. $NaFeO_2 + 2H_2O$ --- $Na^+ + Fe(OH)_3 + OH^-$
3. $2H_2CrO_4 + 6FeSO_4 + 6H_2SO_4 = Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 8H_2O$

Determination of Fe_2O_3 (total) (Volumetry)

Dissolve the residue from the previous operation in hot HCl and precipitate iron as iron hydroxide with NH_4OH. Filter using No.40 filter paper and wash the precipitate 4 or 5 times with hot water. Dissolve the precipitate in hydrochloric acid, boil and reduce it with $SnCl_2$. Cool it immediately. Add 10 ml saturated mercuric chloride solution and 20-25 ml. acid mix and titrate with standard potassium dichromate solution using barium diphenylamine sulphonate as an indicator. Compute the percentage of Fe_2O_3 from the following factor:

1 ml. 1 N$K_2Cr_2O_7$ = 0.07985 g. Fe_2O_3

Note: In Analytical Laboratory, Indian Bureau of Mines, chromite ore was fused with potassium hydroxide in a nickel crucible initially at low temperature and finally to bright red colour with constant stirring. The mass was extracted in water. The soluble was estimated for Cr_2O_3 and insoluble was estimated for Fe. In chromium determination the filtrate can be directly acidified, as the step of removal of H_2O_2 (as in Na_2O_2 fusion) is eliminated, secondly the insoluble can directly be analysed for iron after dissolving in concentrated hydrochloric acid as very negligible amount of nickel is present in the leach. Insoluble, if any, after dissolution of insoluble in hydrochloric acid is again fused with KOH and the extracts are added to respective determinations.

Determination of SiO_2 (Gravimetry)

Take 0.5 g. of finely pulverized sample (all of it should be finer than 200 mesh for fusion) in a platinum crucible and fuse it with Na_2CO_3 at about 1000^oC. Dissolve the fused mass in hydrochloric acid. If black particles remain, filter and wash the residue with hot water 5 or 6 times. Again fuse the residue after ignition with sodium carbonate (2 or 3 fusions are required for complete decomposition of the sample). Keep the solution on the hot plate, dehydrate and bake it for half an hour at 110^oC. Dissolve the baked mass in dilute HCl. Add 50-75 ml water, boil and filter through No.40 Whatman filter paper. Wash the residue with hot water 6 to 7 times. Ignite the residue in a platinum crucible and weigh (W_1) and hydrofluorize the residue by adding 2 or 3 drops of dil sulphuric acid. And 10 ml hydrofluoric acid, ignite and weigh (W_2).

$$SiO_2\ \% = \frac{(W_1 - W_2) \times 100}{W_3}$$

Where -
W_1 = weight of the residue and the platinum crucible
W_2 = weight of the crucible after hydrofluorization
W_3 = weight of the sample taken.

Fuse the residue with sodium carbonate and take it in the filtrate and make up the volume to 250 ml. in a volumetric flask and use it for the determination of CaO & MgO. Follow the procedure given in chapter on determination of major and minor elements from stock solution.

Determination of Aluminium (Gravimetry)

Fuse 0.2 g of finely powdered sample with 3-4 gm sodium peroxide in nickel crucible. Treat the fused mass with approximately 150 ml. of water in 250 ml beaker. Boil vigorously and extract the complete mass. Filter this through Whatman No.40 filter paper in a 500 ml beaker. Wash the residue 5-6 times with hot water. Add 10-15 g. of ammonium nitrate gradually with constant stirring. Boil the content on burner. Filter the aluminium hydroxide thus precipitated through Whatman No.41 filter paper. Wash the precipitate 5-6 times with hot water. Ignite the precipitate at 1000^oC in silica or platinum crucible. Report the mass quantity of alumina (Al_2O_3).

Determination of ferrous iron

Principle

Very finely powdered ore is reacted with a solution of V_2O_5 in a mixture of sulphuric acid and phosphoric acid at a temperature of nearly 400^oC. The un-reacted V_2O_5 titrated with a standard solution of ferrous ammonium sulphate and from the V_2O_5 used up, FeO is calculated.

Reagents

1. **V_2O_5 solution –** Dissolve 18 g. in 500 ml. of water, acidify with H_2SO_4 and make up to the volume of one liter.
2. **$FeSO_4\ (NH_4)_2\ SO_4 6H_2O$(N/10) –** Dissolve 39.20 g. in water, add 5 ml. of 1:1 sulphuric acid and make up the volume to a liter. Standardize against standard N/10 $K_2Cr_2O_7$ solution.

Procedure

Take 0.1 g. of finest possible powder and add 50 ml. of acid mixture (phosphoric and sulphuric acid in the proportion of 4:1). Add 20 ml. of V_2O_5 solution and heat at 350-400^{o}C till the chromite sample is fully digested (3 to 4 hours). Cool and cautiously add nearly 50 ml. of water, and titrate with standard ferrous ammonium sulphate solution using sodium diphenylamine barium sulphonate as indicator. Take a blank of the V_2O_5 solution and from the difference determine FeO.

1 ml. 1 N $FeSO_4(NH_4)_2SO_4\ 6H_2O$ = 0.07185 g. FeO

Note:

1. The determination is difficult and require practice, the strength of acid and temperature should be rigorously controlled to obtain concordant results.
2. Instead of V_2O_5 some workers have used ceric sulphate.

References

1. Shin A.V. – Determination of ferrous oxide in chromite, Zavodskaya Lab. 6, 1199 – 1205 (1937), through Chemical Abstract 32, 1211.
2. Journal of Geochemical Society of India, April, 1967

COBALT ORES

The common minerals are – linnaeite – Co_3S_4, Carroltite – $CuCo_2S_4$ and Cobaltite – CoAsS.

Cobalt is estimated in all nickel ores by the gravimetric method using α nitroso β naphthol reagent.

Determination of cobalt (Gravimetry)

Principle of the method

When α nitroso β napthol is added to a hydrochloric acid solution of cobalt, a brick red precipitate of cobalt nitroso β naphthol, $Co(C_{10}H_6O(NO)_3)$ is formed. Copper, silver, bismuth, tin, chromium, iron, zirconium, titanium, vanadium and nitric acid interfere, but mercury, lead, cadmium, arsenic, antimony, aluminium, manganese, nickel, calcium, manganese, beryllium, zinc and phosphate do not interfere.

Copper and other Group II metals are removed with H_2S and iron together with the other remaining interfering elements is separated with zinc oxide (refer to Volhard's method for manganese under chapter on manganese ore). The cobalt precipitate is ignited and weighed as Co_3O_4.

Reagent

Freshly prepared solution of α nitroso β naphthol 5% W/V in 1:1 acetic acid.

Procedure

Weigh 0.5 to 1 g finely powdered sample in a 250 ml. beaker. Add 10-25 ml. conc. HNO_3, 10-15 ml. conc. HCl and 10 ml. 1:1 H_2SO_4 and a few drops of HF, if necessary, and boil gently over a hot plate and finely evaporate to strong fumes of SO_3. Cool, dilute with water and boil. Adjust the acidity to 5 to 10% with H_2SO_4 and pass a strong stream of H_2S. Filter through No.40 Whatman filter paper and wash the residue thoroughly with acidulated H_2S water. Reject the residue.

Boil the filtrate for 15 minutes to remove H_2S. Add 20 ml. H_2O_2 to oxidize the iron and boil to remove the excess of peroxide. Nearly neutralize with Na_2CO_3 solution and boil to remove all CO_2. Add a suspension of zinc oxide until the precipitate takes the colour of coffee. Boil and filter through No.40 Whatman filter paper with some pulp. Wash 5 to 10 times with hot water. The filtrate will contain only Co, Ni, Mn and a few other elements not affecting the α nitroso β napththol precipitation. (A turbidity of zinc oxide will appear in the filtrate but will dissolve in the subsequent acid treatment).

Add 10 ml. conc. HCl to clear the solution. Dilute the solution to 200 ml. (add enough hydrochloric acid to make a total of 10 ml. in 200 ml. volume). Heat to about 60°C. Add slowly and with constant stirring 1 ½ times, as much reagent as is required by the anticipated cobalt content, with a minimum of 10 ml. in any case. Stir vigorously for one minute. Allow the solution to cool to room temperature for several hours. Filter through No.42 Whatman filter paper, using pulp, and wash the precipitate several times with warm dilute hydrochloric acid (1+9) (if the solution passing through the funnel steam is clear, any precipitate subsequent forming in the filtrate will be free from cobalt). Finally wash the precipitate with hot water until free of chloride.

Transfer the paper and precipitate to a weighed 30 ml. porcelain crucible of deep type. Ignite gently at first and finally to constant weight at 750 to 850°C. Cool in a desiccators and weigh as Co_3O_4.

$$\% \text{ Co} = \frac{\text{Weight of } Co_3O_4 \times 0.7342 \times 100}{\text{weight of the sample taken}}$$

Note: If the determination is done on a high nickel ore, the precipitate may be dissolved in HCl cobalt is reprecipitated.

Determination of Cobalt present in minute quantities (Spectrophotometry)

Principle

The method is based upon the soluble red complex salt formed when cobalt ions react with an aqueous solution of Nitroso-R salt. The cobalt complex is usually formed at pH 5.5 to 6. After the formation of cobalt colour, nitric acid is added and boiled. It decomposes the complexes of most of other heavy metals.

Reagent

Nitroso-R salt – (sodium 1 – nitroso – 2 hydroxy-naphthalene 3, 6 – disulphonate) – 0.2% aqueous solution.

Procedure

Prepare the solution as prescribed for the gravimetric method and take an aliquot or take 0.5 g. of the finely pulverized sample in a vitrosil silica crucible (roast at low temperature if it is a sulphide ore). Add about 2 g. of potassium pyrosulphate and fuse the sample over a low flame. Dissolve the material in hydrochloric acid by boiling. If the sample contains copper, dilute the solution add about 1 g. sodium thiosulphate, boil and filter. If it does not contain copper avoid this step.

Reduce the acidity with ammonia and add pyridine, boil and filter through No.40 Whatman filter paper. Check the pH of the solution. It should be close to pH 6. Add 2 ml. of 0.2% nitroso-R salt, boil for one minute. Add about 2 ml. of conc. nitric acid and boil again for one minute. Cool to room temperature, dilute to 100 ml. in a volumetric flask and determine the optical density at 425 nm against a reagent blank. Determine cobalt concentration with Reference to a working graph prepared by the standard cobalt solution treated in the same manner as the sample solution.

Note :

1. If the sample is siliceous then silica should be removed by dehydration and hydrofluorization.
2. Iron, copper, chromium (III and VI), nickel interfere when present in appreciable quantities.
3. The use of pyridine to precipitate R_2O_3 and control the pH has been developed in the IBM laboratory.

FLUORSPAR

The important commercial source of fluorine is fluorspar or fluorite (CaF_2).

The analysis of fluorspar ores is normally done to determine the following radicals:

$CaCO_3$, SiO_2 R_2O_3 (total oxides), S and P_2O_5, the most important radical is fluorine as CaF_2

Determination of $CaCO_3$ (Gravimetry)

Weigh 1.0 g. of sample and transfer it to a 250 ml beaker. Add 20 ml. 20% (V/V) acetic acid and 100 ml distill water. Heat on a hot plate till it boils. Filter and wash the residue with hot distill water until free from acid. Ignite the residue with filter paper in a platinum crucible at 600°C. Cool in a desiccators and weigh. Loss in weight represents the $CaCO_3$ content.

$$CaCO_3\ \% = \frac{\text{Loss in wt. x 100}}{\text{Wt. of the sample}}$$

Determination of SiO_2 (Gravimetry)

Add to the residue a 15 ml. of 40% hydrofluoric acid (do not add H_2SO_4). Evaporate to dryness. Ignite at 600°C. Cool and weigh. Repeat the acid treatment till there is no further loss in weight. The loss in weight represents the SiO_2 content.

$$SiO_2\ \% = \frac{\text{Loss in wt. x 100}}{\text{Wt. of the sample}}$$

Preparation of stock solution for determination of R_2O_3, CaF_2

Add 1 ml concentrate sulphuric to the mass left after determination of silica in the platinum crucible itself. Fume of the mass carefully. Transfer the crucible to 250 ml beaker. Add 5 ml concentrated hydrochloric acid and 50 ml. DM water. Boil this to extract the mass from the crucible. Turbidity, if any, indicates the presence of BaO (as $BaSO_4$). Filter the solution through Whatman 40 filter paper and make up to 250 ml in volumetric flask.

Ignite the residue and the filter paper in silica or platinum crucible. Weigh the residue and report this as $BaSO_4$.

Determine the other constituent R_2O_3, Al_2O_3, MgO and P_2O_5 as given under the chapter on determination of major and minor constituents. Convert the Ca thus determined to CaF_2 and report as CaF_2 directly. This method gives appreciably accurate estimation of fluorine in turn CaF_2 in fluorspar sample.

More accurate estimation of fluorine can be made by distillation of fluorine as hydrofluosilicic acid and titrating it against thorium nitrate. The procedure is as given below:

Method

When a sample of fluoride is boiled with sulphuric acid + phosphoric acid in the presence of quartz, glass, etc. volatile silicon tetrafluoride is formed. In steam distillation when the steam vapour is used as a carrier gas, the silicon tetrafluoride reacts with water vapour and hexaflurosilicic acid is trapped in a dilute solution of sodium hydroxide. Fluorine in the solution is determined by titrating against standard thorium nitrate solution using sodium alizarine sulphonate as an Indicator.

Procedure

Take 0.1 g. fluorspar, or 1.0 g. of other samples depending on the percentage of fluorine present in it, in a platinum crucible, mix it with 1-2 g. of Na_2CO_3 and fuse it, first on a very low flame and then on just dull red heat. But in a number of cases, even without fusion, the results are quite satisfactory. Extract the mass with 50-100 ml. water and filter. Transfer it to a Kjeldahl flask. Add 75 ml acid mixture and add about 1.0 gm. of sodium silicate or quartzite. Heat the flask on an asbestos sheet making a small hole to expose the bottom of the flask to the flame. When the temperature reaches 140°C, flush the steam and collect the distillate in a NaOH solution (about 25 ml. of 0.1 N). The distillate should be about 300-350 ml. The rate of distillation should be about 5 to 6 ml. in a minute.

Immediately after distillation, make up the volume to 500 ml. and store it in a polythene bottle. Take 20 ml. aliquot for each titration and adjust the strength of $Th(NO_3)_4$ solution, so that the titre value lies in the range 5 to 15 ml. The titration is carried out at pH 2.9 to 3.1 by using monochloro acetic acid (10 ml.) as a buffer and a few drops of alizarine sulphonate as an indicator. A particular shade is very important and has to be decided by the worker himself while doing the standardization of $Th(NO_3)_4$ solution and the sample. Compute the percentage of fluorine from the volume of thorium nitrate used.

The reaction involved is**:**

$$2N_2SiF_6 + 3Th(NO_3)_4 + 7H_2O \longrightarrow 3ThF_4 + 12HNO_3 + 2H_2SiO_3 + H_2O$$

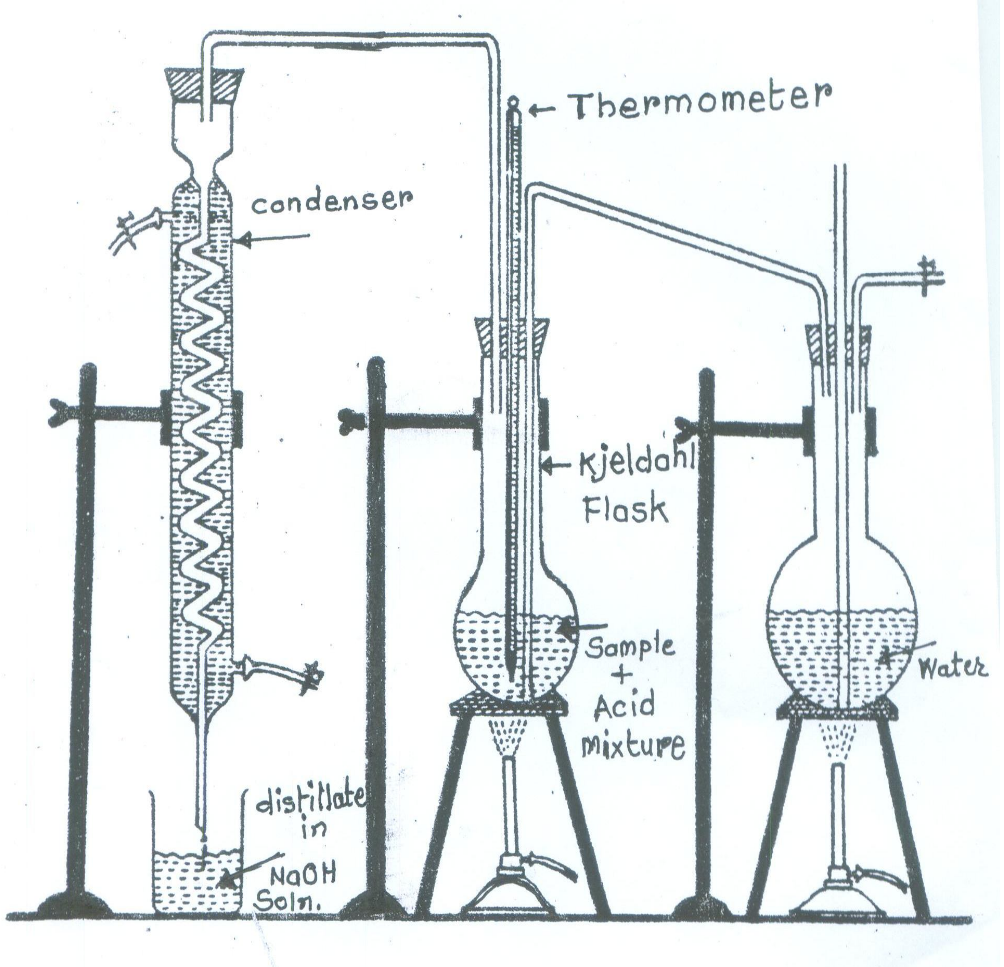
Reagents

1. **Acid mixture**: conc. H_2SO_4 (Sp. Gr. 1.84) + conc. H_3PO_4 (85%) : 3:1 parts, respectively.
2. **Standard thorium nitrate solution (0.025 M).** Weigh 13.806 g. of thorium nitrate $Th(NO_3)_4\ 4H_2O$, dissolve in water and make up to one litre. Mix well, standardize against standard fluoride solution.
3. **Standard sodium fluoride solution**: (1 ml = 1 mg. of F). – Dissolve 2.211 g. of sodium fluoride (AR) previously dried at 120°C to constant weight in one litre of water in a volumetric flask.
4. **Buffer solution** (Monochloroacetic acid pH 2.9 – 3.1). – Dissolve 18.9 g. of monochloroacetic acid in distillled water and dilute to 200 ml, neutralize 100 ml. to phenolpthelein end point with NaOH and add to remaining 100 ml. Dilute to 500 ml. with distill water. Check the pH meter.
5. **Indicator**: Sodium salt of alizarin sulphonate (1:1 aqueous solution).

Notes: All of the solutions used in this experiment should be freshly prepared.
Sulphur and P_2O_5 are determined in the usual way.

Reference

USBM. RI 0314 – fluorine analysis – by H.E. Blake. Indian Standard IS. 2411-1963.



Fluorine distillation apparatus

GYPSUM

Gypsum, $CaSO_4$, $2H_2O$ occurs in nature. The deposits are mainly in less rain fed areas. $CaSO_4.2H_2O$ is fairly soluble in water, especially rainwater. Presence of calcium sulphate imparts permanent hardness to water. Gypsum is analysed for CaO, SO_3, Fe_2O_3, SiO_2, MgO, LOI, Al_2O_3 & $CaSO_4.2H_2O$.

1. **Drying of Gypsum**: Gypsum, $CaSO_4.2H_2O$ is very sensitive to heat. Hence, drying of sample should also be done carefully to avoid loss of water of crystallization. Finely ground powder is dried 45^{o}C for 2 hours. In no case the

temperature should exceed 60°C as it loses one molecule of water of crystallization around 70°C.

2. Loss on Ignition: LOI in gypsum is mainly contributed by the water of crystallization. Moreover this water of crystallization is of greater interest to ascertain the quality of gypsum. Weight about 1 g. of sample in silica crucible. Heat the sample to 250°C in muffle furnace for about 30 minutes. The temperature should preferably below 300°C. Cool the crucible in desiccators. Weigh the crucible and report the loss as loss on ignition.

$$\% \text{ LOI} = \frac{\text{Loss in wt. of the sample x 100}}{\text{Wt. of the sample}}$$

3. Determination of SiO_2 and preparation of stock solution: Weight 0.5 g. of dried sample (at 45°C) in 250ml. beaker. Add 25 ml. of Hydrochloric acid. Digest this on hot plate. Dehydrate and bake the mass at 115-120°C on hot plate. Cool the beaker add 5 ml concentrated hydrochloric acid and 50 ml. DM water. Boil this and filter this through Whatman 40 filter paper. Wash the residue 5-6 times with hot water. Preserve the filtrate. Ignite the residue at 1000°C in muffle furnace in platinum crucible. Cool the crucible in desiccators. Weigh the crucible. Add 2-3 drops of dilute sulphuric acid and 10 ml of hydrofluoric acid. Fume off all acid on an asbestos sheet or low temperature hot plate. Initially heat the crucible at low flame and finally to bright red (1000oC) on a maker burner. Cool the crucible in a desicator and weigh. The loss will correspond to the quantity of silicon dioxide in the sample.

$$SiO_2\% = \frac{\text{Loss in wt. x 100}}{\text{Wt. of the sample}}$$

Fuse the residue left after hydrofluorisation with little ($K_2S_2O_7$) potassium pyrosulphate. Extract the mass into the preserved filtrate by boiling. Cool the solutions and make up this to 250 ml. in volumetric flask.

4. **Determination of CaO, MgO, Al_2O_3, Fe_2O_3**:

Follow the procedure given under the chapter on determination of major and minor constituent from the above stock solution. Estimate CaO preferably by calcium oxalate method if the sample contains phosphate as in phosphogypsum.

5. Determination of SO_3: Weigh 0.2 g of sample in 250 ml. beaker. Add 25 ml. concentrated hydrochloric acid. Digest this on low temperature hot plate for about 30 minutes (till all particles dissolves). Dilute the content of the beaker with 50 ml. DM water. Boil this. Filter this through Whatman 40 filter paper. Collect the filtrate in 500-600 ml beaker. Wash the beaker and residue 5-6 times with hot water. Add 2-3 drops of methylred indicator to the filtrate. Neutralize the filtrate with dilute ammonia. Acidify this with dilute hydrochloric acid. Add 5 ml. in excess. Heat the beaker on burner to boiling. Add 20 ml. 10% barium chloride solution. Continue boiling for 30 minutes. Cool this for 2-3 hours. Preferably the precipitate should be allowed to settle overnight. Filter the precipitate through Whatman 42 filter paper. (To speed up the filtration decant major portion of the solution without disturbing the precipitate). Wash the precipitate 5-8 times with small fraction of cold water. (till it is free from Ba^{++} ions). Transfer the filter paper along with precipitate to a silica or platinum crucible. Ignite the precipitate at 800°C. The carbon of filter paper should preferably be burned below 600°C. Add 2-3 drops of dil. H_2SO_4 and ignite this finally at 800°C. Weigh the content. This corresponds to $BaSO_4$.

$$SO_3\,\% = \frac{\text{Wt. of } BaSO_4 \text{ ppt x 100 x 0.3430}}{\text{Wt. of the sample}}$$

6. **Determination of $CaSO_4.2H_2O$**: Weigh 1 g. of sample in 500 ml. beaker. Add 100 ml (10%) alkaline ammonium acetate solution. Maintain the alkalinity with phenolphthalein and dil. Ammonia through out the experiment. Digest this on water/steam bath for about 1 hr. Filter this through sintered glass crucible (porosity G3) under suction. Transfer the residue completely to the crucible. Wash the crucible 5-6 times with cold water. Heat the crucible to a constant weight at 100°C. Find the weight of residue. The loss will correspond to the quantity of $CaSO_4$ 2H2O (more precisely $CaSO_4$ x H_2O).

$$CaSO_4.2H_2O = \frac{\text{Loss in wt. x 100}}{\text{Wt. of the sample.}}$$

IRON ORES

The important minerals that constitute iron ore are hematite (Fe_2O_3) and magnetite (FeO, Fe_2O_3). Other associated minerals are hydrates of iron like goethite, limonite, etc.

The radicals determined in iron ores are Fe (total) FeO, Fe_2O_3, Al_2O_3, CaO, MgO, SiO_2, TiO_2, P, S, and LOI.

Determination of SiO_2 (Gravimetry)

Take 1 g. of sample in a 250 ml. beaker add 30 to 35 ml. conc. hydrochloric acid. Digest the mixture on a hot plate. Evaporate to dryness and bake the mass for one hour at 100 to 115°C. Cool the mass and take up with about 10-ml. conc. hydrochloric acid in about 100-ml. water, boil the solution and filter hot through Whatman filter paper No.40. Wash the residue thoroughly with hot water containing a little hydrochloric acid till no yellow colour remains. Finally wash it with hot water only.

Ignite the residue in a platinum crucible at 950°C to a constant weight, cool in a desiccators and weigh (W_1). Add 5-8 drops (1:1) H_2SO_4 to the residue and then 10-15 ml. HF. Evaporate slowly over a low heat (at the end copious fumes are seen leaving a dry mass). Ignite the residue over a flame to a constant weight, cool in a desiccators and weigh the crucible (W_2).

$$\%\ SiO_2 = \frac{(W_1 - W_2) \text{ x } 100}{\text{Wt. of the sample taken}}$$

Where:

W_1 = weight of the platinum crucible with the material before hydrofluorization
W_2 = weight of the platinum crucible after hydrofluorization

Fuse the residue in a platinum crucible with potassium pyrosulphate. Dissolve the fused mass in water containing HCl by heating and add this solution to the main filtrate. Take the solution in a 250 ml. volumetric flask and make the volume up to the mark and take aliquots for the determination of other radicals. Follow the procedure given in chapter on determination of major and minor constituent from stock solution.

Determination of ferrous iron (Volumetry)

Principle

Ferrous iron is determined by dissolving powdered ore in hydrochloric acid in the absence of air and titrating with standard $K_2Cr_2O_7$ solution.

Procedure

To a 500 ml. conical flask, fit a rubber stopper carrying a long inlet tube and a short outlet tube. Have a ready source of carbon dioxide from a Kipp's apparatus. Accurately weigh by difference into the conical flask about 0.5 g. of powder ore and connect the inlet tube for CO_2 and displace the air in the flask by a current of carbon dioxide. Now add to the flask 25-ml. 1:1 hydrochloric acid**,** quickly replacing the stopper. Dissolve the sample by heating the flask over a wire gauge, meantime passing a slow stream of carbon dioxide. Heat till there are not black particles (some insoluble siliceous matter may be observed). Now cool the flask and the contents in running water while still passing carbon dioxide. When cool, dilute the solution to nearly 150 ml. with cooled distilled water containing no dissolved oxygen. Add 50 ml. of a mixture of sulphuric and phosphoric acids. Titrate the ferrous iron by standard N/10 potassium dichromate solution using few drops of barium diphenylamine sulphonate as indicator to a violet end point.

Repeat the experiment to obtain concurrent results and calculate the percentage of ferrous iron from –

1 ml. 1 N $K_2Cr_2O_7$ = 0.07185 g. of FeO.

LIMESTONE, DOLOMITE, MAGNESITE AND ALLIED MATERIALS

Calcium is a widely distributed element occurring in nature in the combined state. It occurs as carbonate, sulphate, phosphate, fluoride, and silicate and in a larger number of complex compounds associated with silicon, iron, aluminium, boron, titanium, sodium and potassium.

The main calcium minerals of commercial importance are calcite ($CaCO_3$), dolomite ($CaCO_3$>$MgCO_3$), magnesite ($MgCO_3$) and gypsum ($CaSO_4.2H_2O$).

Determination of silica (Gravimetry)

Weigh accurately 1 g. of dried sample in a 250-ml. beaker and add 10 ml dilute hydrochloric acid (cover the beaker to prevent loss by effervescence) and 1 ml. conc. nitric acid. Expell all acid. Bake the mass at 100-115^{o}C for one hour. Dissolve the mass in 5 ml concentrated HCl and 50 ml water by boiling. Cool and transfer all the residue in the beaker as well as that adhering to the sides of the beaker to a filter paper by hot water, finally with a rubber policemen or a piece of moist filter paper. Wash the residue first with 1% hot hydrochloric acid till all yellow colour disappears and finally wash with hot water till free from chloride ions. Preserve the filtrate for further determinations. Transfer the residue into a platinum crucible and burn and ignite the filter paper at 900 to 950^{o}C. Cool in a desiccators and weigh. Now moisten the residue with a few drops of 1:1 sulphuric acid and add to it about 20 ml hydrofluoric acid. Evaporate to dryness, ignite, cool and weigh again. The difference will be the SiO_2 (lost as SiF_4 by volatilization).

Calculation :

$$\text{Silica \%} = \frac{(W_2 - W_3) \times 100}{W_1}$$

Where –

W_2 =weight of platinum crucible with residue before hydro-fluorization

W_3 =weight of the platinum crucible with residue after hydro-fluorization,

W_1 =weight of the sample taken.

Preparation of Main Solution

Fuse the residue left over in the platinum crucible after hydrofluorization of silica with potassium pyrosulphate and extract it in dilute hydrochloric acid and add the extract to the filtrate reserved for further processing. Take the solution in a 250 ml. volumetric flask and make up to the volume and mix well (if the filtrate is bulky, reduce the volume by boiling). Aliquots are taken for other determinations. Follow procedure given in chapter on determination of major and minor constituent from the stock solution.

MANGANESE ORE

The common minerals constituting our manganese ores are psilomelane ($Ba_3(OH)_6\ Mn_8O_{16}$), pyrolusite (MnO_2) and braunite ($3Mn_2O_3.MnSiO_3$).Other associated manganese minerals are manganite, jacobsite, hausmannite, sitaparite, manganese bearing garnets like spessartite, etc.

Manganese ores are generally analysed for Mn, MnO_2, SiO_2, Al_2O_3, Fe_2O_3, FeO, P, BaO, CaO, MgO and LOI.

Determination of silica (Gravimetry)

Outline

The sample is decomposed with hydrochloric acid in the presence of an oxidizing agent like nitric acid. The solution is evaporated to dryness and the residue baked. SiO_2 is determined by hydrofluorisation.

Procedure

Take one g. of the sample in a 250 ml. beaker, add 5 ml conc. nitric acid and 25 ml. conc. hydrochloric acid, evaporate slowly over a hot plate to dryness, dehydrate and bake for 15 to 20 minutes. Cool the beaker and add 10 ml. conc. hydrochloric acid and 50 ml. water and boil. Filter through No.40 Whatman filter paper. Wash the residue first with hot 1% hydrochloric acid till no yellow colour remains and transfer the residue with the filter paper into a clean platinum crucible, burn off the filter paper and finally ignite the residue. Cool in a desiccators and weigh (W_1). Add few drops of 1:1 sulphuric acid and about 20 ml hydrofluoric acid and keep over an asbestos board having a flame underneath and slowly evaporate to dryness, then ignite over a bare flame. Cool in a desiccators and weigh (W_2).

$$\% \, SiO_2 = \frac{(W_1 - W_2) \times 100}{\text{Wt. of the sample taken}}$$

Fuse the residue in the platinum crucible with sodium carbonate, dissolve in dilute hydrochloric acid and mix with the filtrate. Take in a volumetric flask and make up to the volume with water and take aliquots for subsequent determinations. Follow the procedure given in chapter on determination of major and minor constituents from the stock solution.

Determination of CaO and MgO

Take 50 ml aliquot in 250 ml beaker. Add 2-3 g. of ammonium chloride and ammonia. Add 2-3 ml of bromine water. Boil this solution, cool and filter through Whatman 41. Wash the residue 5-6 times with hot water. Now again add 2-3 ml of dilute ammonia and 2-3 ml of bromine water. Precipitate manganese left, if any. Filter this through Whatman 41. Wash the residue 5-6 times with hot water. Repeat treatment with bromine water till all manganese is precipitated. Divide this filtrate into two parts estimate calcium in one part and magnesium in other as explained under the chapter on determination of major and minor element.

Determination of manganese dioxide (Sodium oxalate method) (Volumetry)

Outline

The sample is treated with a known excess of standard sodium oxalate solution in the presence of sulphuric acid. The remaining oxalate is titrated with standard permanganate solution. The equivalent manganese dioxide is calculated from the quantity of oxalate consumed.

Reaction involved

$MnO_2 + H_2C_2O_4 + 2H^+ = Mn^{++} + 2\ CO_2 + 2\ H_2O$

Reagents

1. **Standard sodium oxalate solution 0.1 N**
2. **Dilute sulphuric acid 4% (V/V).**
3. **Standard potassium permanganate solution 0.1 N.**

Procedure

Take 0.2 to 0.5 g. of the sample in a conical flask; add 50-ml. standard sodium oxalate solution to which 20 ml. dilute sulphuric acid has been added. Digest over a steam bath till it is almost free from black particles make the volume to 100 ml. with hot water (temperature of the solution – 70-80°C), titrate with standard potassium permanganate solution.

Take a blank of an equivalent amount of the standard sodium oxalate solution that has been added to the sample and from the difference compute the percentage of MnO_2 present as follows:

1 ml. 1 N $KMnO_4$ = 0.04347 g. MnO

Calculation

$$MnO_2 = \frac{(A - B) \times C \times 0.04347 \times 100}{D}$$

Where –

A = volume in ml. of standard permanganate solution required for the blank,
B = volume in ml. of standard permanganate solution required for the excess of the sodium oxalate,
C = normality of the standard permanganate solution, and
D = weight in gm. of the sample.

Determination of FeO in Mn ore by Iodine Monochloride Method (Volumetry)

Reagent

1. **Iodine solution** Dissolve 10 gm of KI and 6.44 gm. of KIO_3 in 25 ml water and 75 ml of concentrated HCl. Little carbontetra chloride is added to the bottle after shaking CCl_4 should be pale violate. If it is colourless add dil. KI drop by drop till free I_2 is present. While CCl_4 is distinctly coloured add dil KIO_3 till it is decolourised after shaking.
2. **KIO_3 Standard Solution** : Dissolve 5.35 gm of dry KIO_3 in water and dilute to volume in 1 litre flask. This is M/40 or 0.1 N solution.
3. **Conc.HCl**
4. **Boric Acid**

Procedure

1 gm of powdered sample is taken in Pt crucible or dish and excess of ICl solution (1 ml of ICl solution = 0.4 M = 3% FeO) is added. Concentrated HCl (20 ml) is added and the mixture is stirred with Pt rod. After some time, add 10 ml of 40% AR HF. Cover the vessel with suitable lid from the beginning. After 5 minutes, pour the content in 250 ml conical flask containing 2 gm of Boric Acid 50 ml conc. HCl. Dilute the solution to about 150 ml. Then add 10 ml of CCl_4 stopper the bottle and shake for about 20 seconds. After this stage CCl_4 layer, which is deep purple colour due to liberated I2, is seen. This is obscured if carbonecious matter is there together at interface. Titrate the solution by adding KIO_3 with intermitant shaking of the bottle until the purple colour almost disappears from the organic layer. Add further CCl_4 in which the end point can be easily detected by disappearing of purple colour. Towards the end of titration shake the contents of the bottle, after addition of each drop of KIO_3 solution.

$$\mathrm{2Fe^{2+} + I_2\, 2Fe^{+3} + 2I'} \longrightarrow \qquad \mathrm{2Fe^{2+} + I_2} \longrightarrow \mathrm{2Fe^{+3} + 2I}$$

$$\mathrm{I_2 = 2Fe}$$

It should be noted that the total solution should contain atleast 30% conc. HCl by volume.

MOLYBDENUM ORES

The principal minerals of molybdenum are molybdenite – MoS_2, wulfenite – $PbMoO_4$ and powallite – $CaMoO_4$.

Determination of molybdenum (Volumetry)

Principle

The procedure depends upon the reduction of hexavalent molybdenum to the trivalent form by passing an acidified solution of it through a column of amalgamated zinc. The reduced molybdenum compound is sensitive to atmospheric oxygen hence, the reduced compound is caught in an excess of ferric solution in an atmosphere of CO_2. An equivalent amount of ferrous ion is formed. Titration of the reduced solution by means of standard permanganate establishes the amount of molybdenum.

Procedure

Weigh 0.2 to 0.5 g. of finely pulverized (-100 mesh) sample depending on the grade of ore in a nickel or iron crucible and add approximately 5 times its weight of sodium peroxide, and mix with a dry glass rod. Heats over a low flame to obtain a clear melt. Keep the melt over the low flame and swirl the crucible form time to time till no black particle is left un-attacked this generally takes 5 to 10 minutes. Cool the crucible and place it in a 500 ml. beaker and pour nearly 200 ml. distill water and boil, remove the crucible and wash well with water, pouring the washings into the beaker.

Filter through No.40 Whatman filter paper and wash the residue 5 times with hot water (excess washing should be avoided). Discard the precipitate. Neutralize the filtrate with 1:1 H_2SO_4 and add 20 ml. in excess.

Activate the Jones reductor by passing through it about 400 ml. of 4% H_2SO_4. Discard the washings. Place in position a 500 ml conical flask containing 25 ml. of 10% ferric ammonium sulphate solution and 5 ml. orthophosphoric acid. CO_2 is passed through the flask having an inlet and outlet for the CO_2 gas. Then pass the solution through the reactor at a slow rate such that 2 or 3 drops fall per second into the conical flask. At the end, wash the reductor several times with 4% H_2SO_4 catching all the washings into the conical flask. Pass a stream of CO_2 throughout the operation.

Remove the conical flask add 2 ml. of phosphoric acid and titrate against standard $KMnO_4$ solution to a pink and point which should persist for at least 5 seconds.

Calculate MoO_3 percentage from the following factor :

1 ml. 1N $KMnO_4$ = 0.0320 g. of Mo

The reactions involved are:-

1. $2MoO_4^- + 3\,Zn + 16H^+ = 2Mo^{+3} + 3Zn^{++} + 8H_2O$
2. $3Fe_2(SO_4)_3 + Mo_2(SO4)_3 + 8H_2O = 2H_2MoO_4 + 6H_2SO_4 + 6FeSO_4$
3. $MnO_4^- + 5Fe^{++} + 8H^+ = Mn^{++} + 5Fe^{+++} + 4H_2O$

Reagents

1. **Ferric Ammonium Sulphate** 200 g. Ferric Ammonium Sulphate
   1760 ml distilled water 40 ml H_2SO_4
2. **Potassium permanganate** – N/10.

Alternate method for decomposition of the ore

The procedure mentioned above is suitable for all types of ores. The following method is suitable for wulfenite and molybdenite:-

Dissolve 0.5 g. of powdered ore by treatment with 25 ml. of fuming nitric acid and 5 ml of sulfuric acid in a 500 ml covered beaker at a temperature just short of boiling. Evaporate until fumes of SO_3 are expelled freely. Cool, add 50 ml water and boil. Filter through No.40 Whatman filter paper. The residue consists of lead sulphate, silica and possibly contains small amount so under-composed ore, tungstic and molybdic acids. Save both the residue and the filtrate.

Dissolve the lead sulphate from the residue in hot ammonium acetate solution by washing. Ignite the siliceous residue in a platinum crucible and remove silica by treating it with sulphuric and hydrofluoric acids. Fuse the residue with potassium pyrosulphate and mix with the filtrate. Precipitate R_2O_3 with ammonia and filter. Dissolve the precipitate in sulphuric acid and reprecipitate R_2O_3 with ammonia and filter. Collect the two filtrates containing all the molybdenum in a beaker. Then proceed with the solution as above.

Note on application and limitation of Jone's reductor

1. The ferric ammonium sulphate should be tested to ensure that all the iron is present in the trivalent state. If all the iron is not in the trivalent state, drops of $KMnO_4$ solution are added till a pink colour is obtained (excess should be avoided). The solution is boiled and if the pink colour persists, a drop of conc. HCl is added when the colour will disappear.
2. A blank is determined for the Jone's reductor as follows and deducted from the $KMnO_4$ burette readings: 25 ml ferric ammonium sulphate and 5 ml phosphoric acid are placed in the conical flask, as stated in the experiment, which is then attached to the apparatus and about 300 ml water containing 4% H_2SO_4 solution is passed and titrated with $KMnO_4$. The blank so determined should not be more than 0.3 to 0.5 ml.
3. Sulphuric acid is generally used as usage of hydrochloric acid may interfere in the subsequent titration, e.g. with potassium permanganate**.**
4. Nitric acid must be absent. If nitric acid is present and 3-4 ml of sulphuric acid and evaporate until fumes of SO_3 are evolved. Repeat the operation to ensure complete removal of nitric acid.
5. Organic matter must be absent.
6. Solution containing compounds of copper, tin, arsenic, antimony and other reducible metals must never be present. If present, they must be removed before the reduction by treatment with hydrogen sulphide..
7. Ions which are reduced in the reductor to a definite valency state are those of titanium to Ti^{+++}, chromium to Cr^{++}, molybdenum to Mo^{+++}, niobium to Nb^{+++} and vanadium to V^{++}, uranium is reduced to a mixture of U^{+++} and U^{++++}.

Preparation of amalgamated zinc for reactor

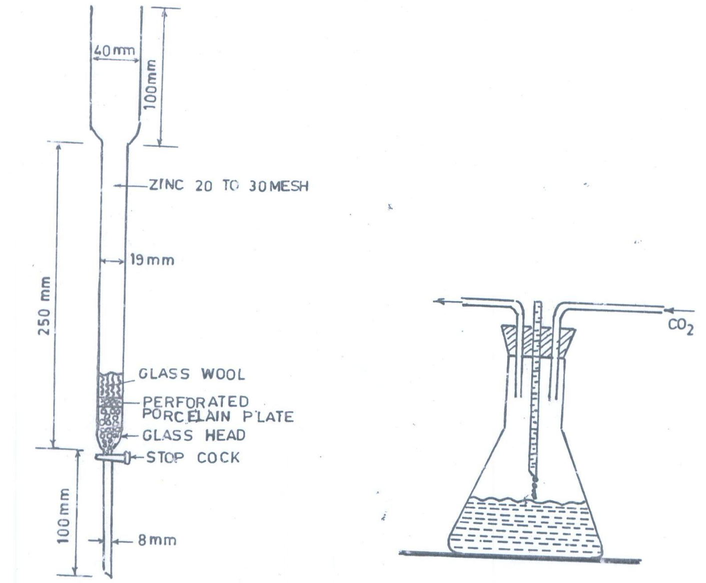
About 300 gm. of AR Zinc, minus 10 +20 mesh size, is covered with 2 percent mercuric chloride solution in a beaker. The mixture is stirred for 5-10 minutes and then the solution is decanted from the zinc and washed three to four times with water by decantation. The resulting amalgamated zinc should have a bright silvery lustre.

The ideal amalgam should give rapid and complete reduction with minimum of hydrogen evolution**.**

The reductor containing amalgam is always kept filled with enough water to cover the surface, otherwise basic salt will form which will tend to clog the column.

Note

1. The quantity of $HgCl_2$ required will be such as to yield Hg equivalent to 1-5% of the zinc used.
2. Use –10, +20 mesh zinc metal. Finer material will clog the reactor.



2 Cms IN DIAMETER
20 40 Cm LONG
20 MESH ZINC AMALGAMATED
WITH 0 1 TO 5% MERCURY

JONES REDUCTOR

Determination of minute amounts of Molybdenum (Spectrophotometry)

Principle of the method

Molybdenum (VI) in acid solution when treated with a suitable reducing agent in the presence of a little ferrous iron is converted largely into molybdenum (V). This forms a complex with thiocyanate ion probably largely due to formation of Mo $(SCN)_5$, which is red in colour. The latter may be extracted with oxygenated solvents. The colour depends upon acid concentration (optimum concentration 1 N) and the concentration of the thiocyanate ion (2 to 10%). The complex has maximum absorption at 460 nm.

Reagents

1. **Potassium thiocyanate**, 10%
2. **Stannous chloride –** 10 g. of dihydrate in 100 ml. of 1 N hydrochloric acid.
3. **Ferrous ammonium sulphate** – 1 gm in 100 ml. of 0.2 N. sulphuric acid.
4. **Isoamyl alcohol**.

5. **Standard solution –** Dissolve 0.075 g of Ar MoO_3 in dilute sodium hydroxide, dilute with water, make slightly acidic with hydrochloric acid, and make up to 500 ml wit water.
   1 ml = 0.0001 g Mo
   = 0.1 mg Mo

Procedure

1. If a solution has already been made, proceed with an aliquot for the determination of Mo. Otherwise prepare the solution as follows and proceed

2. Fuse 0.1 g of finely ground sample with 0.5 g of sodium carbonate in a platinum crucible. Digest the cake in water containing a few drops of alcohol until completely disintegrated. Filter through No.40 Whatman filter paper. Wash the residue with hot water. Reject the residue, take the filtrate which contains molybdenum as sodium molybdate and acidify with hydrochloric acid and proceed as follows

Transfer the solution to a separating funnel and add 1 ml of 1% ferrous ammonium sulphate solution and 3 ml. of 10% potassium thiocyanate and 2 ml. of 10% stannous chloride solution. After 30 seconds, add exactly 25 ml amyl alcohol, shake vigorously for 2 minutes and allow the coloured phase to separate. Discard the aqueous phase and take the clear amyl alcohol phase in the cell of a spectrophotometer and measure the absorbance at 460 nm and determine the percentage of Mo from the standard curve prepared from a known solution. Run a reagent blank throughout.

Reference

1. E.B. Sandell, Colorimetric Determination of Traces of Metals. Interscience Publishers Inc., New York, 1959 p. 641.

NICKEL ORES

The principal nickel bearing minerals are pentlandite (Ni, Fe)S, garnierite (Ni, Mg) $SiO_4 .nH_2O$, and niccolite (NiAs). Nickel is also found associated with copper ore deposits. In India, Nickel is found associated with laterites in Sukinda, Orissa.

Determination of nickel

Procedure

A. Sulphide ores

Take 0.5 to 1 g. of the finely pulverized sample in an iron crucible and fuse with sodium peroxide. Dissolve in hydrochloric acid and pass H_2S to precipitate members of the second group. Filter and wash the residue with water saturated with H_2S. Boil the filtrate vigorously to remove H_2S, add bromine water and boil to oxidize iron to the ferric condition. Nearly neutralize with ammonium hydroxide and finally with pyridine to precipitate iron and boil to coagulate. Filter through No.40 Whatman filter paper. Wash the residue with hot ammonical water five to six times. Acidify the filtrate with hydrochloric acid and add 10 ml of 10% dimethylglyoxime heat and make it ammonical. Keep over a boiling water bath for two hours and then keep the precipitate overnight. Filter through a weighed sintered glass crucible, wash with cold water and then dry the precipitate at 150^{o}C. Cool in a desiccators and weigh.

$$\text{Ni \%} = \frac{\text{Weight of the nickel DMG complex x 0.2031 x 100}}{\text{Weight of the sample taken}}$$

B. Oxidized ores

Take 0.5 to 1 g of sample in a beaker, and add 15 to 20 ml conc. hydrochloric acid and 5-10 ml nitric acid, dry and dehydrate the sample. Take with hydrochloric acid boil and filter. Ignite the residue in a platinum crucible and hydrofluorise the residue. Fuse the residue with potassium pyrosulphate and dissolve in hydrochloric acid and add to the mother liquor. If copper is present, remove it with H_2S. Add bromine water and boil to oxidize the iron. Add 2 g. of tartaric acid to prevent the precipitation of the hydroxides of iron, aluminium and chromium by ammonium hydroxode. Then slowly make it ammoniacal to ascertain if complexing is complete, i.e. no precipitate should appear in the ammoniacal medium. If a precipitate appears, acidify the solution, add more tartaric acid and again add ammonium hydroxide. The solution must remain clear at this point. Add hydrochloric acid until the solution is very slightly acidic, heat to 60 to 80^{o}C and then add 10 ml of 10% alcoholic solution of dimethyl glyoxime. Add ammonia solution till a faint smell is perceptible and then add a slight excess. Keep over hot water bath for two hours and then keep the precipitate overnight. Filter through a weighed sinter glass crucible wash the precipitate with cold water. Dry the precipitate at 150^{o}C and weigh. Compute the Ni % as above.

Reaction involved

$$Ni^{++} + 2H_2\,DMG = Ni^*\,(HDMG)_2 + 2H^+$$

- $Ni(C_4H_7N_2O_2)_2$

Note:

1. Ensure that iron is in the trivalent condition and that no excess oxidizing agent is present.
2. If the final precipitate is bulky and blackish in colour, filter and dissolve the residue in hydrochloric acid and reprecipitate nickel under similar conditions.
3. If iron and alumina are very high and complexing with tartaric acid is not very efficient i.e. even after the addition of a large amount of tartaric acid, the precipitate appears when made ammoniacal, then, R_2O_3 should be removed by pyridine, (Reference: No.2).
4. The Sukinda nickel ores contain chromium and as such not fully attacked by acid. Fuse the finely ground ore with sodium peroxide in an iron crucible and extract with water and filter. Wash the residue with hot water five or six times. The filtrate will contain sodium chromate and is rejected. Dissolve the residue in hydrochloric acid and proceed for the

determination of nickel.

References

1. G.E.F. Lund ell, H.A. Bright and J.I. Hoffman – Applied Inorganic Analysis, John Wiley and Sons, Ney York, 1959 – p. 409.
2. A.K. Ray at. Al. – Use of Pyridine as A Precipitant in Gravimetric Estimation of Nickel and Cobalt in Low Grade Ores, Indian Journal of Technology, 1969, Vol. 7 No.4 pp, 129-130.

Determination of minute amount of nickel (Spectrophotometry)

Principle

The sample is brought into solution by treating with nitric, hydrochloric and hydrofluoric acid. Iron, aluminium, etc. are complexed with sodium citrate. To the ammonical solution dimethyl glyoxime is added and the red nickel dimethyl glyoxime complex is extracted with chloroform. The chloroform is stripped off the nickel complex in acid medium, treat with bromine water and make to a suitable volume in a volumetric flask and the absorbance measured at 445 nm.

Reagents

1. **Dimethyl glyoxime (sodium salt) –** 1% in water.
2. **Sodium citrate –** 1-% - Dissolve 100 g. in 100 ml water.
3. **Chloroform –** A.R. grade
4. **Bromine water –** Saturated.

Procedure

(A) **Preparation of Solution** – Weigh 0.5 to 1 g. of the sample in a beaker add 5 ml of conc. or fuming nitric acid and 25 ml of conc. hydrochloric acid. Digest and dry over a hot plate. Cool the beaker add 10 ml of conc. hydrochloric acid and about 50 ml of water, boil, filter through No.40 Whatman filter paper. Wash the residue with hot water. Take the filter paper along with the residue in a platinum crucible and slowly burn off the filter paper. Add few drops of 1:1 sulphuric acid and about 20 ml hydrofluoric acid, evaporate, dry and finally ignite the residue. Fuse the residue with potassium pyrosulphate, extract in hydrochloric acid and mix with the filtrate. Add 10 ml of sodium citrate solution, heat for 10 minutes and then allow to cool. Neutralize the solution with aqueous ammonia (1:1), boil and, if any, precipitate, filter through No.40 Whatman filter paper. Wash the residue with ammoniacal sodium citrate solution. Make up the volume 250 ml.

(B) **Formation of complex and extraction**: Transfer 50 ml of the solution to a separatory funnel and add 1 ml of conc. ammonium hydroxide, adjust the pH at 7.5. Add 3 ml of 1% dimethyl glyoxime solution. Extract the red compound with chlorororm.

Shake the chloroform extract vigorously with 5 ml portion of 1 M HCl. Transfer the aqueous layer to a 50 ml volumetric flask. Add 1 ml saturated solution of bromine water and 2 ml conc.aqueous ammonia. Add 1 ml of 1% dimethyl glyoxime solution and dilute to volume, stand for 5 minutes and measure the absorbance at 445 nm. Obtain the percentage of nickel in the sample by Reference to a graph prepared from the standard nickel solution.

Note :

1. Copper may accompany the nickel in the extraction. But most of the copper is removed from the chloroform extract when it is shaken with ammonia solution, whereas the nickel remains in the organic solvent. The nickel dimethyl glyoxime in the chloroform layers may be decomposed by shaking with dilute hydrochloric acid. Most of the diemthyl glyoxime remains in the chloroform layers. The nickel is transferred to the aqueous phase.
2. Much manganese may interfere but this is prevented by adding hydroxyl-ammonium chloride, which maintain the element in the divalent state.
3. Citrate or tartarate is added to prevent the precipitation of iron, aluminium, etc.

Reference

Arthur I. Vogel – A Textbook of Quantitative Inorganic Analysis, 3rd Edition, 1962.
The English Language Book Society, pp. 794.

COPPER-LEAD-ZINC (POLYMETALLIC) ORES

Copper minerals viz. chalcopyrite, cuprite, vallerite, Dioptase, Chrysocolla, etc.zinc minerals sphalerite, Marmatite, Hemimozphite, willenite, etc. and lead minerals galena, cerussite, Anglesite, Barysilite, etc. are easily attacked by a mixture of hydrochloric and nitric acid. This is finally converted to sulphate by addition of sulphuric acid mainly for two reasons, firstly to destroy all nitrate, which interferes in copper estimation by iodometry, secondly to convert lead into lead sulphate, which remains as insoluble residue and it is determined from the residue.

The above procedure for analysis of Cu-Pb-Zn, polymetallic ore is developed in Indian Bureau of Mines and successfully used for analysis of ore dressing products of these ores.

A) Determination of Silica & Preparation of Stock Solution

1. Take 1 g of the sample in a beaker, add 20 ml conc. hydrochloric acid, heat this on hot plate for 30 minutes, add 10 ml conc. nitric acid. Keep over a hot plate and when the brisk reaction subsides, add 5 ml 1:1 sulphuric acid, evaporate and fume to dryness.
2. Treat the resultant dry mass with 10 ml 1:1 sulphuric acid and make the volume to nearly 100 ml. with water, boil over a hot plate and filter thoroughly No.40 Whatman filter paper. Wash the residue with hot water containing a few drops of sulphuric acid.

Preserve the filtrate for estimation of Cu, Zn, CaO, MgO, Fe, Al_2O_3, etc.

Transfer the insoluble lead sulphate and other insoluble above the original beaker. Add 100 ml 5.5 pH mixture of ammonium acetate and acetic acid to this.

Boil this for 15 minutes. Filter this through Whatman 40 filter paper wash the residue with hot ammonium acetate-acetic acid buffer 3-4 times with hot water. Determine Pb in the filtrate as given in the chapter of on determination of major and minor constituent from the stock solution.

Ignite the filter paper and residue in platinum crucible at 1000°C. Cool the crucible in desiccators and weigh. Add 2-3 drops of dilute sulphuric acid and 10-15 ml 48% hydrofluoric acid. Heat this on asbestos sheet to fume off all acid slowly. Heat the crucible initially on a low flame and finally to a blast flame. Cool this in desiccator and weigh. Loss will correspond to silica in the sample.

Fuse the residue after hydrofluorisation with potassium pyrosulphate and extract this in the preserved filtrate. Make up the solution 250 ml in volumetric flask. Determine the other radicals from this stock solution as per the procedure given in chapter on determination of major and minor radicals from stock solution.

B) Determination of Graphitic Carbon

Weigh 2 g of sample in 250 ml beaker. Add 25 ml concentrated hydrochloric acid. Digest for 30 minutes to expel hydrogen sulphide gas. Now add 5 ml concentrated nitric acid and continue digestion for 30 minutes. The content of the beaker must not dry add occasionally concentrated hydrochloric acid. Dilute this with 100 ml water. Filter this through sintered glass crucible of porosity G_4. Wash this 3-4 times with hot water. Finally give 2 washings with 10 ml carbon-disulphide to dissolve precipitated sulphur, if any. Dry the crucible at 105°C for 30 minutes. Cool the crucible in desiccator. Weigh the crucible. Find the weight of insoluble material. Remove the material carefully on a glaze paper/plastic sheet. Mix this well. Part this into two parts. Determine volatile matter and ash as given in chapter on coal.

% Graphitic Carbon =100-(%VM +% Ash). Correct the % of graphitic carbon by a factor (% of insolubles/100).

PYRITES

Determination of pyrite (FeS_2)

Take 1 g. sample in a beaker and add 25 ml conc. HCl and digest for about fifteen minutes (pyretic sulphur is insoluble in conc. HCl). Filter through No.40 Whatman filter paper and wash the residue with hot water. Ignite the residue in a silica crucible and dissolve in conc. HCl. Reduce with $SnCl_2$, when hot, cool it and add 10 ml mercuric chloride. Make the volume to nearly 200 ml. with water add 25 to 30 ml. of sulphuric phosphoric acid mixture and titrate with N/10 potassium dichromate solution using few drops of barium diphenylamine sulphonate as an indicator. Calculate percentage of iron. From iron calculate S and FeS_2 as follows:

Fe % x 1.143 = S % Pyrite
Fe % x 2.1483 = FeS_2 %

NOTE:

The above method is only empirical and arsenopyrite (FeAsS) and chalcopyrite ($CuFeS_2$), if present, will also be counted as pyrite.

ROCK PHOSPHATE AND APATITE

The primary sources of phosphorus and its compounds are phosphate rock and apatite. They are usually analysed for moisture, LOI, CO_2 SiO_2, Al_2O_3, P_2O_5, Fe_2O_3, CaO (free), CaO (total), MgO and F.

Determination of SiO_2 and preparation of stock solution for CaO, Al_2O_3, Fe_2O_3

Weigh accurately 1 gm (W) of sample in a beaker. Add 15 to 20 ml. conc. HCl and 5 ml. conc. HNO_3, digest over a hot plate and evaporate to dryness. Add about 50 ml. of water and boil. Filter through No.40 Whatman filter paper. Wash the residue five to six times with hot water. Preserve the filtrate. Take the residue along with the filter paper in a platinum crucible, burn off the filter paper and ignite the residue.

Moisten the residue with 5 drops of 1:1 H_2SO_4 and add 10 ml. hydrofluoric acid, evaporate to dryness and finally ignite at a red hot temperature, cool in a desiccators and weigh (W_2). Fuse the residue with sodium carbonate and mix with the filtrate. Take the filtrate in a 250 ml. volumetric flask and make up to the volume. Use this solution for the determinations of Fe_2O_3, Al_2O_3, CaO.

$$\% \, SiO_2 = \frac{(W_1 - W_2) \times 100}{W}$$

Where –

W = weight of the sample
W_1 = weight of the crucible and contents before hydrofluorization, and
W_2 = weight of the crucible and contents after hydrofluorization.

Note:

If the phosphorite contains fluorine, some silica will be lost in the above process. In such case, proceed for the determination of silica in presence of fluorine as given in chapter on Alumino Silicates. If the fluorine content is very less, then the lengthy process may be avoided. Alternatively, take 1 g of sample 250 ml beaker cover the sample with 1 g boric acid; add 25 ml concentrated hydrochloric acid. Heat this on hot plate to expel all acid. Dry and dehydrate the mass. Moisten the mass with 1-2 ml concentrate hydrochloric acid and 50 ml of DM water. Boil the content. Filter this through Whatman 40. Wash the residue 5-6 times with hot water. Ignite the residue in platinum crucible at $1000^{o}C$. Estimate silica by hydrofluorisation.

Determination of total CaO

Take an aliquot equivalent to 0.1 g. in a beaker, add 0.05 gm. of citric acid, boil, and add 25 ml. saturated solution of ammonium oxalate solution and few drops of bromophenol blue indicator. Add ammonia until a dirty blue colour develops (pH 3.5), boil and allow the precipitate to settle for at least two hours.

Filter through No.40 Whatman filter paper; wash the residue with hot water till free from oxalate ions (test with $KmnO_4$ and a drop of 1:1 H_2SO_4). Dissolve the residue in 10 ml 1:1 sulphuric acid 50 ml DM water, heat to 70-80^oC and titrate hot with 0.1 N $KMnO_4$ solution to a permanent pink colour. Compute the percentage of total CaO from the following factor:-

1 ml. 1 N $KMnO_4$ = 0.028 g of CaO

Determination of Fe_2O_3 and Al_2O_3

Follow the procedure given under the chapter on determination of major and minor elements.

Determination of magnesium (Gravimetry)

Procedure

Weigh 1 g sample in 250 ml beaker add 25 ml conc. HCl and 5 ml conc. nitric acid. Reduce volume to 10 ml, add 5 ml. H_2SO_4 (1:1) and evaporate to fumes. Cool, wash down the walls of the beaker with jets of water and evaporate again until all fumes are evolved. Cool and add 100 ml. absolute methyl or ethyl alcohol. Stir well and allow tostand for 2 to 3 hours, preferably overnight filter through No.40 Whatman filter paper under suction and wash residue 5 or 6 times with absolute alcohol.

Evaporate the filtrate on a steam bath as fast as possible and make up the volume to 100 ml. Add 2 gm. of citric acid and 15 ml. of 25% solution of diammonium hydrogen phosphate. Make alkaline to litmus by adding ammonium hydroxide and add 50 ml. conc. ammonium hydroxide in excess. Shake vigorously, let settle for 4 hours or overnight in a cool place. Filter using Whatman No.42 and wash with very dilute ammonium hydroxide (1:10). Dissolve the precipitate in hot dil-HCl and repeat the process to obtain a pure precipitate. Ignite the precipitate at 1000^oC and weigh as $Mg_2P_2O_7$.

$$\% \text{ MgO} = \frac{\text{Wt. of } Mg_2P_2O_7 \text{ x } 0.3623 \text{ x } 100}{\text{Wt. of the sample}}$$

Determination of free CaO (volumetry)

Take 0.5 gm. of sample in a volumetric flask, add 25 to 30 gm. cane sugar and about 200 ml. water, shake occasionally for 2 hours and make up the volume.

Take an aliquot equivalent to 0.1 gm. of sample and titrate with N/10 oxalic acid solution using phenolphthalein as indicator. Compute the percentage of CaO from the following factor:

1 ml. 1 N oxalic acid = 0.025 g. of CaO

Determination of P_2O_5

Weigh 0.05 to 0.1 g. of finely pulverized material in 500 ml. conical flask, add 10 ml concentrated hydrochloric acid and digest over a burner till complete dissolution takes place, add 2 ml con. HNO_3 and again digest for about 10 minutes.

Neutralize with NaOH solution till a faint precipitate appears and add 2 ml. of conc. hydrochloric acid, make the volume to nearly 120 ml. Add 0.5 g. of citric acid, heat to boiling, then add 30 ml. citromolybdate solution, again heat it to boiling and add from a burette in a thin stream 25 ml quinoline hydrochloride solution, and again boil for 5 to 10 minutes. Allow the precipitate to settle at least three hours. If time permits, it is better to keep it overnight. Filter through a pad of paper pulp under suction. Wash the precipitate with 30 ml. portion of cold water letting each washing run through before applying the next, until the washings are acid free (test for acidity with litmus paper about six washings are required). Transfer the precipitate to the original flask; add N/10 NaOH solution in multiples of 25 ml. from a pipette till the precipitate dissolves completely. Add 5 or 6 drops of thymol blue or phenolphthalein indicator and titrate the excess of alkali with standard N/10 HCl to the appropriate end point. Take a blank for 25 ml. of NaOH and comparing with this find out the exact volume of NaOH used up by the precipitate. Compute P or P_2O_5 from the following factors:

1 ml. of 1 N HCl = 0.001193 g. of P
= 0.002733 g. of P_2O_5

Reaction involved:

$$(C_9H_7N)_3H_3PO_4, \quad 12\ MoO_3 \quad + \quad 26\ NaOH \longrightarrow Na_2HPO_4 + 12\ Na_2MoO_4 + 3C_9H_7N \ +14H_2O$$

SELENIUM AND TELLURIUM

Se & Te are separated by hydrazine in 9.5 N HCl solution. The method is based on the interaction of selenious acid with excess standard solution of thiosulphate.

$$4Na_2S_2O_3 + H_2SeO_3 + 4\ HCl = Se + 2Na_2S_4O_6 + 4NaCl + 3H_2O$$

The unreacted thiosulphate is titrated with iodine solution.

Tellurium is determined by the reaction between tellurous acid and excess potassium iodide.

$$H_2TeO_3 + 4I^- + 4H^+ \quad = \quad Te + 2I_2 + 3H_2O$$

Small quantities of Se & Te are reported in the presence of collecting agent Hg_2Cl_2

Reagents

1. **HNO_3 density** 1.42 g/Cu cm.
2. **Mixture of bromine & carbon tetrachlorid**e (2:3)
3. **H_2SO_4 conc**.
4 **HCl density 1.19 g/cu cm. 5% of solution diluted 2:1000, Hg_2Cl_2, solution containing 1 mg Hg in 1 ml.**
5. **Stannous chloride,** crystalline $SnCl_2.2H_2O$ and 20% in 20% HCl
6. **Hydrazine hydrochloride,** 10% solution**.**
7. **Sodium Thiosulphate**, 0.02 N solution
8. **Iodine** 0.02 N solution
9**.** **KI 0_3%** solution

Procedure

Take 1 to 5 g of fine sample in 600 ml beaker, add 8-25 ml of a mixture of bromine & carbon tetrachloride and allow to stand for 10-20 minutes. Add 10-50 ml of HNO_3 by small portion with stirring and allow the solution to stand in the cold. Then heat carefully and evaporate to a small volume. After the sample has been decomposed, add 10-40 ml of H_2SO_4 and evaporate the solution to H_2SO_4 fumes. Cool the residue, add a small amount of water and evaporate to H_2SO_4 fumes. Repeat this operation until all nitrogen oxides and organic substances are completely removed.

Dissolve the residue 60-200 ml of water and 10-15 ml HCl with boiling in a beaker (covered with glass) for 5-10 minutes. Add HCl to adjust its concentration 15% (V/V). Heat the solution to boil. Add 5 ml of mercurous chloride and reduce the ferric iron by small portion of $SnCl_2$, when the solution becomes colourless, add 3-10 ml of the reductant in excess, a small amount of paper pulp, boil for 5 minutes and allow to stand for 10 minutes at a temperature about the boiling point. Separate the selenium and tellurium ppt. On a paper pulp filter and wash 3-4 times with hot HCl (2:100).

Separation of Selenium and Tellurium

Place the selenium and tellurium ppt back in the precipitation beaker; add 20-25 ml conc. HCl and 4-5 drops of HNO_3. Loosen the filter and heat on water bath to dissolve the ppt (the filter whitens). Add 40 ml conc. HCl and 50 ml of water, heat the solution almost to boil and add 15-20 ml hydrazine solution. Stir the mixture and allow to stand for 4 hours in warm place. Separate the selenium ppt on double filter and wash 7-8 times 5% HCl.

To isolate tellurium, dilute the filtrate with water to 250 ml, add a small quantity of filter pulp, heat to the boil, add 0.3 g of $SnCl_2.2H_2O$ and boil until solution fully clears. Separate the precipitated tellurium on double filter and wash 7-8 times 5% HCl.

Determination of Selenium

Transfer the selenium ppt from filter paper into beaker, add 10 ml conc. HCl, loosen the filter by glass rod, add 3-4 drops HNO_3 and heat the mixture on water bath to dissolve the ppt completely. Add 150 ml water and 4 g of carbamide and boil for 2-3 minutes. Cool the solution at room temperature and 25 ml 0.02 N solution thiosulphate and titrate its excess with iodine solution in the presence of starch.

Determination of Tellurium

Transfer the tellurium ppt from the filter paper into a flask, add 10 ml conc. HCl and 3-4 drops HNO_3 and heat on water bath to dissolve the ppt. Completely cool the solution, add 10 ml Kl solution and titrate excess iodine with sodium thiosulphate solution in the presence of starch until the blue or dark cherry solution (depending on the tellurium content) turns pale yellow.

SILICA

Determination of minute amounts of silica (Spectrophotometry)

Principle

Silicic acid reacts with a solution of molybdate in the acidic medium to give an intense yellow coloration due to formation of complex silicomolybdic acid $H_4(SiMo_{12}O_{40})$ which can be measured at 400 nm wavelength. It is better to reduce the complex acid to molybdenum blue. A solution of hydroquinone, aqueous sodium sulphide, ferrous sulphate, etc. is generally used. But in the I.B.M. Laboratory, the reduction is done by ascorbic acid. After reduction, the absorbance can be measured at various wavelengths. For optical density, 600 nm is preferred in our work.

Reagents

1. **Ammonium molybdate solution 12% W/V** – Dissolve 120 g of AR ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}$) in water and dilute to one liter. Allow the solution to stand for one day and filter.
2. **Oxalic acid solution 5% W/V** – Dissolve oxalic acid 50 g in 500 ml. water and dilute to one liter. Filter the solution, if necessary.
3. **Ascorbic acid 2% W/V** – Prepare fresh solution as required.
4. **Standard solution of silica** – Fuse 0.1 gm. of pure silica with 0.5 g. of anhydrous sodium carbonate in a platinum crucible, cool the melt. Dissolve it in water and dilute to 1000 ml and store in a polythene bottle.

   1 ml. = 0.1 mg of SiO_2

Procedure

Preparation of solution

A. If the sample is in solution, dilute the solution.

B. If silica is present in a solid sample, weigh 0.1 gm of the sample in a platinum dish and add about 10 ml. of conc.hydrochloric acid and keep over a hot plate and evaporate (do not dry). Dilute to 50 ml. with water, add 1 ml. hydrochloric acid, boil and filter through No.40 Whatman filter paper. Wash the residue with hot water. Take the filter paper in a platinum crucible, char the paper and ignite the residue. Fuse the residue with sodium carbonate, dissolve in conc.hydrochloric acid and mix with the filtrate. Take the solution in a volumetric flask, make up the volume and draw an aliquot for the determination of SiO_2. Proceed as below :

C. Alternatively, take 0.1 gm. of the sample in a nickel crucible, add a few pellets of sodium hydroxide and a pinch of sodium carbonate. Heat the crucible over a hot plate for about 15 minutes followed by fusing over a flame at dull red heat. Cool the crucible and extract the sodium silicate formed with boiling water. Filter through No.40 Whatman filter paper and wash the residue with hot water. Take the filtrate into a volumetric flask and take an aliquot for the determination of SiO_2.

Complex formation and measurement

Transfer 25 ml. of an aliquot to a 100 ml volumetric flask and add 2 ml 10% nitric acid. Then add 5 ml. of 12% ammonium molybdate solution and allow it to stand for 5 minutes to complete the complex formation. Now add 10 ml. of 5% oxalic acid solution, 5 ml. of 25% sulphuric acid and 5 ml of 2% ascorbic acid solution in rapid succession, and mix thoroughly after each addition. Allow the solution to stand for about minute and dilute with water. Run a blank simultaneously and measure the absorbance of the sample against the reagent blank solution at 600 nm. Determine the silica from the standard calibration curve.

Note:

1. This method in various modifications has been used for the determination of silica in fresh water, sea water in boiler fed water, iron ores, ferrous alloys and steel.
2. Phosphorus (V) and arsenic (V) form similar yellow heteropolymolybdate complex under the conditions employed for the formation of yellow – silico-molybdic acid complex. Interference from phosphorus and arsenic is eliminated by the destruction of this complex with oxalic acid prior to the reduction of silicon complex.

Reference

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TIN ORE

Cassiterite (SnO_2) is the chief ore of tin.

Determination of tin (Volumetry)

Principle

Finely ground ore is fused with sodium peroxide in a zirconium or iron crucible and the sodium stannate thus formed is dissolved in hydrochloric acid. Tin is reduced to the stannous form by lead foil by boiling in an atmosphere of carbon dioxide and the reduced tin is titrated with standard iodine solution using starch as indicator.

Reagents

1. **Standard N/10 – iodine solution** – Weigh about 12.692 g of iodine and 26 g of potassium iodide in a 500 m. beaker and agitate with about 400 ml water until they dissolve. Wash the contents into a one liter graduated flask and make up to the correct volume. Standardize this solution against a standard $Na_2S_2O_3$ solution to find out the exact normality.
2. **Starch solution** – Mix about 1 g of soluble starch with about 20 ml cold water and add the mixture slowly to 80 ml boiling water. Boil for a few seconds. Prepare fresh solution when required.

Procedure

A Take 0.1 to 0.5 g of the finely ground (-200 mesh) sample in an iron or zirconium crucible (see note 1) according to the anticipated amount of tin in the sample and add about 8 times its weight of sodium peroxide.

Mix the constituents either with a dry glass or platinum rod. Sprinkle a thin layer of peroxide over the top of the mixture and heat gently over a low flame at a temperature just sufficient to produce complete fusion. A slow gradual fusion is more successful and avoids loss due to spattering. Keep the melted mass at a dull redness for about 5 minutes and with the aid of tongs give the crucible a swirling motion several times during that period.

Remove from the heat and allow it to cool. Then, with the aid of a glass rod, upset the crucible in about 100 ml water in a 500 ml beaker and cover with a watch glass to prevent loss due to spattering. When the disintegration and solution of the fused mass is complete, remove and wash off the crucible with water. Add concentrated hydrochloric acid until the precipitate has dissolved. The solution of the sample should be complete. If any un-decomposed material is present, the determination should be started again. There may be some iron scales from the crucible but this can be ignored. Filter the solution through no.40 Whatman filter paper and wash the filter paper with hot water.

B. Alternatively, the fused mass is boiled with water and filtered (see Note 2) through No.40 Whatman filter paper. The residue is washed with hot water and the filtrate containing tin as sodium stannate is taken for reduction and determination after acidifying with hydrochloric acid.

Transfer the acid solution (either of A or B) in a 500 ml conical flask, add 50 ml conc. hydrochloric acid, about 10 ml of 1:1 sulphuric acid and 15 gm granulated lead or lead foil. Boil the solution for about an hour in an atmosphere of carbon dioxide to reduce the Sn^{4+} to Sn^{++} state (see Note 3). Remove the flask from the heat and put it in a cool water bath and cool rapidly while maintaining the carbon dioxide atmosphere. When the flask and its contents are cooled, remove the stopper and rinse it off into the flask (see Note 4), add a few ml. of starch solution and titrate immediately with N/10 iodine solution. The end point is a faint permanent blue tinge. Compute the percentage of tin from the following factor:

1 ml of 1N iodine = 0.05935 g of Sn.

Take a blank in each batch of operation starting from the fusion stage and determine the iodine consumed and deduct this blank from each titration (see Note 4).

Reaction involved

$$SnCl_2 + I_2 + 2\,HCl \longrightarrow SnCl_4 + 2HI$$

NOTES :

1. The sample should be finely ground to –200 mesh, the accuracy of the analysis depends largely upon it.
2. The sample may be fused with sodium peroxide and the aqueous extract containing tin as sodium stannate taken but there are chances of the bulky precipitate holding up tin ions or entrapment of tin due to hydrolysis, this may give a low result.
3. After reduction with lead, the colour of the solution will be white. It may reasonably be assumed that all the Sn has been reduced if the solution is boiled for 40 to 50 minutes.
4. A blank should be taken from the very start of the operation of each batch and the consumption of iodine determined and deducted from each titre value.
5. Water contains dissolved oxygen and hence it should be removed by boiling when used for washing the conical flask during titration.
6. It is not necessary to remove excess lead prior to titration with iodine since lead has no effect on the cold solution.
7. If the solution turns blue, brown or purple during reduction, the presence of tungsten, molybdenum or vanadium is indicated. In such a case, tin is to be precipitated by passing H_2S gas in an acidic solution, filtered and ignited and fusion with sodium peroxide proceeded with.

TITANIUM BEARING ORES

The principal minerals of titanium are Ilmenite ($FeO.TiO_2$) and Rutile (TiO_2).

Determination of TiO_2 (Volumetry)

Reagents

1. **Standard ferric ammonium sulphate $Fe_2(NH_4)_2(SO_4)_4.3(H_2O)$ Solution –** Dissolve 60 g of the salt in 600 ml distilled water acidified with 20 ml of 1 : 1 H_2SO_4. Add $KmnO_4$ solution until a pink colour begins to appear. Dilute the solution to 2 litres. Standardize against a 0.1 N $K_2Cr_2O_7$ solution to find out the exact strength.
2. **Indicator** – Dissolve 24 g of NH_4CNS in 100 ml water.
3. **Aluminium foil** – Commercial grade is satisfactory.

Preparation of solution of the sample

Treat 0.2 gm of finely powdered (-200 mesh) ore with 10 to 25 ml of a mixture of sulphuric and hydrofluoric acids (1:5), add a few drops of HNO_3 and evaporate the solution to fumes to expel HF. If a residue remains upon dissolving with water containing a little sulphuric acid, filter and fuse it with $K_2S_2O_7$, dissolve in H_2SO_4 and mix with the filtrate.

Alternatively, take 0.2 gm of sample in a silica crucible add approximately 1 gm of potassium pyrosulphate and fuse over a low flame till no black particle remains. When cool, dissolve in 1:1 sulphuric acid and water and make up in a 250 ml volumetric flask and proceed with an aliquot for the determination of TiO_2 .It hydrolyses easily and as such the acid strength in the volumetric flask should be approx. 5%).

Procedure

Take the solution in a wide-mounted 500 ml conical flask with a 2-hole rubber stopper. Add 25 ml conc. HCl. Add a strip of aluminium foil to the flask (nearly 2 gm), close with the rubber stopper and through one hole pass a slow stream of CO_2 from a Kipp's apparatus, using the other hole as an outlet. The solution in the flask should be boiled to clarify it and expel the excess H_2 (boil for at least half an hour). All the while, a slow stream of CO_2 is to be maintained. When cool, remove the stopper and the delivery tube. Add 5 ml ammonium thiocyanate solution as an indicator and titrate quickly with $FeNH_4(SO_4)_2.12H_2O$ solution to a faint red colour. Run a blank and deduct this reading from the main reading. Calculate TiO_2 from the following factor :

$$1 \text{ ml } 1 \text{ N } FeNH_4(SO_4)_2.12H_2O = 0.08 \text{ g } TiO_2$$

Note :

Reduction Procedure

1. The titanium solution should not contain more than 0.15 gm of TiO_2 with 10-15%H_2SO_4 and it should have a volume of 125 ml.
2. Reduction with aluminium will not take place unless HCl is present.

Reactions involved

a. $6\,Ti(SO_4)_2 + 2Al = 3Ti_2(SO_4)_3 + Al_2(SO_4)_3$
b. $Ti_2(SO_4)_3 + Fe_2(SO_4)_3 = 2\,Ti(SO_4)_2 + 2\,Fe_2SO_4$

The ionic reactions are:

$$6\,Ti^{++++} + 2\,Al \longrightarrow 6Ti^{+++} + 2\,Al^{+++}$$

$$Ti^{+++} + Fe^{+++} \longrightarrow Ti^{++++} + Fe^{++}$$

Determination of silica (Gravimetry)

Principle

The sample is fused with potassium pyrosulphate. The melt is dissolved and evaporated with sulphuric acid to fumes, diluted and filtered. Residue is fused with sodium carbonate and the melt dissolved, evaporated to dryness and baked. The residue is ignited and the silica is determined by the loss in the weight after volatilization with hydrofluoric acid.

Procedure

(a) Transfer 0.5 g of the finely pulverized ore in a platinum crucible containing about 3 g of potassium pyrosulphate, heat it at a low temperature to get a clear melt. Remove the crucible from the heat, and allow it to cool to the room temperature.

Transfer the crucible with its content to a beaker and extract it with 100 ml 1:1 sulphuric acid. When the fused mass is completely dissolved, remove the crucible washing down with 1:1 sulphuric acid and evaporate the solution to copious fumes, cool, add nearly 150 ml of dilute sulphuric acid, boil and filter through No.40 Whatman filter paper. Wash the precipitate in the filter paper with hot dilute sulphuric acid and finally with hot water. Preserve the filtrate and washing in a beaker. Transfer the filter paper along with the residue to a platinum crucible and ignite.

(b) Fuse the residue in the platinum crucible with about 1 gm of sodium carbonate, dissolve the cake in hydrochloric acid, evaporate to dryness and dehydrate. Take up in 1:1 hydrochloric acid, boil and filter. Wash the residue with hot dilute hydrochloric acid and finally with hot water.

Take the filter paper along with the residue in a platinum crucible, burn off the filter paper and ignite the residue. Cool in a desiccators and take the weight W_1. Add few drops of 1:1 sulphuric acid and about 20 ml of hydrofluoric acid. Evaporate to dryness, ignite, cool and weigh W_2. From the difference of weight, compute the percent of silica. Fuse the small amount of residue left in the platinum crucible with potassium pyrosulphate, take up with 1:1 sulphuric acid and mix with the solution reserved in operation (a). Make up the volume in a 250 ml volumetric flask and take aliquots for the determination of Fe_2O_3, Al_2O_3, Mn, Cr_2O_3, etc. Follow the procedure given in chapter on determination of major and minor constituent from the stock solution.

Determination of FeO (Volumetry)

Principle

The very finely pulverized ore is decomposed with sulphuric acid and hydrofluoric acid in CO_2 atmosphere. Boric acid is added to fix the excess hydrofluoric acid as fluoboric acid. The solution is titrated with standard $KMnO_4$ solution.

Procedure

Pulverize the sample in an agate mortar to the finest possible size, irrespective of the grain size of the sample supplied. Weigh 0.2 g of the sample for concentrates and middling and 0.5 g for tailings in a corning or pyrex brand 500 ml conical flask. There should be an arrangement for the inlet and outlet of CO_2 through a rubber bung fitted with the conical flask. Put the flask over a very low flame and put the CO_2 delivery tube on and add the following solutions in sequences and swirl from time to time.

1. Add 30 ml 1:3 H_2SO_4 and simmer over the flame for 15 minutes.
2. Add 10 ml HF, simmer over the flame for 10 minutes and swirl the flask from time to time.
3. Add 10 ml 1:3 H_2SO_4 and simmer for 15 minutes.
4. Add 3 ml HF, simmer for 5 minutes and swirl from time to time.
5. Add 5 ml 1:3 H_2SO_4 and maintain a mild heat do not heat to SO_3 fumes.

Allow the solution to cool in an atmosphere of CO_2. Dilute to nearly 200 ml with oxygen free water add about 4-5 g. of boric acid and remove the CO_2 delivery tube add 2 ml of phosphoric acid and titrate with N/10 $KMnO_4$ solution to a faint pink end point. Calculate the percentage of FeO from the following factor:

1 ml 1 N $KMnO_4$ = 0.07185 g FeO

TUNGSTEN ORES

The important tungsten-bearing minerals are Wolframite $(FeMn)WO_4$ and Scheelite ($CaWO_4$). In the IBM Laboratory, the gravimetric method is used for ores and ore dressing products containing high tungsten values up to 5% WO_3 . Spectrophotometric method is employed for low tungsten values below 5% WO_3.

Determination of WO_3 (Gravimetry)

Pulverise the sample in an agate mortar until it is minus 200 mesh.Weigh 0.1 to 0.5 gm of the sample, according to the anticipated amount of WO_3 content and add 70 ml. conc. hydrochloric acid and digest over a hot plate at a low temperature till all black particles dissolve (about 3 hours). Add 20 ml conc. nitric acid to the very hot boiling solution, digest and evaporate to about 50 ml. Make the volume to nearly 100 ml. with hot water. Stir thoroughly and gently simmer the solution. Add 10 ml cinchonine hydrochloride solution (10 gm. of cinchonine dissolved in 100 cc of 6 N HCl) and boil over the hot plate. Allow it to settle and filter through no.40 Whatman filter paper adding a little pulp. Wash the precipitate 3 times with 0.1% cinchonine hydrochloride solution. Dissolve the precipitate in the same beaker in hot conc. ammonia to convert all the tungsten acid to ammonium tungstate. Filter through No.41 Whatman filter paper and wash the residue with hot water. Take the filtrate and boil until all free ammonia is expelled and dilute the solution to 100 ml with hot water. Add to the boiling solution 50 ml conc. HCl and 25 ml conc. HNO_3 and boil. Add 10 ml cinchonine hydrochloride solution and 50 ml hot water and again boil.

Allow it to cool at room temperature. Filter through No.40 Whatman filter paper and wash the residue as before.

Ignite the precipitate in a weighed platinum crucible. The temperature should not exceed 750°C (WO_3 is volatile above this temperature). Cool the ignited oxide and moisten with a few drops of water. Pour a few drops of HF and keep over a low heat to remove silica. When dry, heat to a dull red temperature (not exceeding 750°C). Weigh as WO_3. The residue should have a lemon yellow colour.

$$WO_3\ \% = \frac{\text{Weight of the ignited residue x 100}}{\text{Weight of the material taken}}$$

Sources of error

In the gravimetric determination of tungsten, the following points should be remembered.

1. Good results can be obtained only by careful work and strict adherence to all details from the preparation of the sample to the final weighing as WO_3.
2. The representative sample of ore should be thoroughly dried and ground to minus 200 mesh.Complete decomposition of the ore might not be obtained if a coarse sample is used.
3. Volatilization of the silicon with HF before the final weighing is a must, failure to remove the silica invariably gives high results.
4. A reaction of about 3 hours is required for Scheelite ores.

Determination of small amount of Tungsten (Spectrophotometry)

This method is based on the formation of a yellow tungsten thiocyanate complex after reduction of tungsten with stannous chloride in an approx. 1.8 M sulphuric acid and 2.3 M hydrochloric acid medium. Tungsten is determined by direct spectrophotometric measurement at 400 nm of absorbance of the complex in an aqueous medium.

Reagents

1. **$SnCl_2$ 2 M** – Dissolve 113 gm of $SnCl_2$ (AR), dihydrate in conc. HCl and make up to 250 ml with conc. HCl.
2. **Tartaric acid** in one liter of water.
3. **Potassium thiocyanate (20%)** – Dissolve 20 g of potassium thiocyanate in 100 ml water. This reagent should be prepared fresh daily.

Procedure

Weigh 0.1 to 0.2 gm of finely pulverized sample in a silica crucible or hard test tube. Add 0.5 to 1 gm of potassium pyrosulphate, mix well and fuse to a clear red hot melt and keep in this condition for at least 10 minutes, remove from the flame and allow it to cool. Dissolve the cake by boiling with 40-50 ml of 0.5 M tartaric acid. filter the resultant solution through No.40 Whatman filter paper. Wash the residue with hot water containing a pinch of tartaric acid. To the filtrate, add 10 ml conc.

H_2SO_4, 20 ml. of 12 N HCl and 5 ml of 2 M stannous chloride solution. Place the beaker in a boiling water bath for half an hour. Add 10 ml water, mix and finally cool the beaker to 10-15°C (ice-cold water bath).

Add 10 ml of 20% potassium thiocyanate solution and take the solution in a 100 ml volumetric flask and make up the volume with distilled water. Allow it to stand at room temperature for 10 minutes. Determine the optical density of the solution immediately at a wavelength of 400 nm or using a blue filter, if colorimeter is used, against a reagent blank. Calculate the percentage of WO_3 from the calibration curve prepared by using standard tungsten solutions.

References

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Determination of Silica & preparation of stock solution for Tungsten, Molybdenum, Niobium, Tantalum ores

Weigh 0.5 g. of sample in 500ml. beaker. Add 50 ml. concentrated hydrochloric acid and 10 ml. concentrated nitric acid. Heat this on high temperature hot plate; continue addition of small portion of HCl and HNO3 till all black particles dissolves. If the sample contains black silicate minerals such as horn blend all black particles will not disappear, 4-5 hours digestion is sufficient. Drive off all nitric acid by addition of small portions of hydrochloric acid and heating this continuously on hot plate. Finally dry, dehydrate and bake the mass. Extract the mass in 5ml. conc. hydrochloric acid and 50ml. water. Filter this carefully through Whatman 40 filter paper. Wash the beaker and the residue 2-3 times with small volume of hot water. Preserve the filtrate. Dissolve the residue along with filter paper in dilute ammonia and water in the same beaker by boiling. Filter through, Whatman 40 filter paper. Wash the residue 3-4 times with water containing little ammonia. Finally wash the residue 2-3 times with hot water. Ignite the residue in platinum crucible at 1000°C. Cool this in desiccators and weigh. Add 2-3 drops of dilute sulphuric acid and 10-15 ml. hydrofluoric acid.Heat this on asbestos sheet on a low flame or low temperature hot plate to expel all acid. Heat the crucible initially on a low flame and finally at a blast flame at 1000°C. Cool the mass in desiccators and weigh. The loss corresponds to the quantity of silica in the sample.

$$\% \text{ Silica} = \frac{\text{Loss in weight x 100}}{\text{Weight of the sample}}$$

Fuse the residue with potassium pyrosulphate. Extract the mass in the preserved filtrate by boiling. Follow the procedure given in the chapter on determination of major and minor constituents from the stock solution for determination of Ca, Mg, Fe, Mn, TiO_2, Al_2O_2, etc.

Determination of Sulphur in Tungsten, Molybdenum, Niobium and Tantalum samples:

Weigh 0.2-0.3 g. of sample in 250ml. beaker, add 5ml. bromine water, 25 ml. concentrated hydrochloric acid and 5 ml. nitric acid. Heat this on hot plate to reduce the volume to 5 ml. Sample must not dry. Add 50 ml. DM water. Filter this through Whatman 40. Wash the residue 5-6 times with hot water containing dil.hydrochloric acid. Collect the filtrate in 250ml. beaker. Add 2-3 g. of finely cut aluminium foil or granulated zinc to reduce iron. Heat the solution. Filter through Whatman 41 filter paper. Collect the filtrate in 500ml. beaker. Neutralise the filtrate with dil. Ammonia and reacidify the solution. Add 5 ml. of dil. Hydrochloric acid in excess. Make volume to about 250 ml, add 20 ml. 10% barium chloride solution, boil the content for 5 minute. Cool for 3-4 hours, preferably overnight. Decant the major portion of liquid without disturbing the precipitate. Finally filter the precipitate through Whatman 42 filter paper. Wash the precipitate 5-6 times with cold water. Ignite the precipitate along with the filter paper at 1000^{o}C. Weigh the precipitate of BaSO4.

$$\% \text{ Sulphur} = \frac{\text{Wt. of } BaSO_4 \text{ ppt } \times 100 \times 0.1374}{\text{Wt. of the sample.}}$$

VANADIUM ORES

Vanadium is widely distributed in nature, being found in ores, hard coal, limestone, bauxite, phosphorite, etc. Usually, the amount of vanadium present is extremely small. The following are the more important vanadium minerals, vanadinite (PbCl) Pb_4 (VO_4), carnotite $K_2O.2UO_3.V_2O_5$ and titaniferous vanadium ores.

Determination of chromium and vanadium (Volumetry)

Principle

A solution of vanadium is reduced with ferrous ammonium sulphate and vanadium is preferentially oxidized with potassium permanganate at room temperature so as not to oxidize any chromium, which might be present. The excess permanganate is reduced with sodium nitrite. Urea is added to decompose excess nitrite and vanadium is titrated with standard ferrous ammonium sulphate using diphenylamine barium sulphonate as indicator.

Reagents

1. **Sodium nitrite – 3.5 g/l**
2. **Ferrous ammonium sulphate 0.1 N –** 39.216 g/l Standardize against a 0.1 N $K_2Cr_2O_7$ solution.

Procedure

Fuse 0.2 to 0.5 gm of finely ground ore with 5 times its weight of sodium peroxide in an iron or nickel crucible. Transfer into a 500 ml beaker, add water and boil. Filter through No.41 Whatman filter paper, adding some pulp. Wash with hot water. Reject the residue and proceed with the filtrate. Vanadium in the form of sodium vanadate will pass into the solution. Boil the solution for 30 minutes to expel H_2O_2. Transfer into a 500 ml. beaker, neutralize with (1:1) H_2SO_4 and then add 4-6 ml. in excess.

Add ferrous ammonium sulphate solution until a drop of the solution shows blue in a spot test with potassium ferricyanide solution. Add 10-15 ml. H_3PO_4 (to prevent Fe interference) and cool to room temperature. Add N/10 $KMnO_4$ until a slight pink colour is obtained. Let it stand for 2 or more minutes to make sure that all vanadium is oxidized. Then destroy the excess $KMnO_4$ with 0.05 N $NaNO_2$ solution. Add 2 gm. of urea and stir. Then, allow it to stand for 5 minutes. Add 15 gm. of sodium acetate and stir to dissolve. If a precipitate is formed, add a drop of H_2SO_4 to clear it. Add 8 drops of diphenylamine barium sulphonate indicator, allow 2 or 3 minutes for the full colour of the indicator to develop. Titrate with 0.10 N ferrous ammonium sulphate until the disappearance of blue colour. Calculate V or V_2O_5 from the following factor:

1 ml of 1 N $Fe(SO_4).(NH_4)_2SO_4$ = 0.05094 g. V
= 0.09094 g. V_2O_5

NOTE: The maintenance of a uniform sulphuric acid concentration of 5 to 7% at the start of the titration and a uniform speed of titration for all samples are essential.

Determination of small amounts (less than 0.5%) of Vanadium (Spectrophotometry)

Principle

In approximately 0.5 N sulphuric acid medium, vanadium forms a yellow phosphotungstovanadic acid complex which can be measured at 400 nm.

Reagents

1. **Sodium tungstate 0.5 N –** Dissolve 16.5 g. of $Na_2WO_4.2H_2O$ in water and dilute to 100 ml.

2. **Standard vanadium solution –** Dissolve 1.785 g. of pure V_2O_5 previously ignited at 500°C in slight excess of sodium hydroxide, add slight excess of sulphuric acid and dilute to one litre. this solution contains 1 mg. of vanadium per ml.

Procedure

Fuse 0.1 to 0.2 gm of the sample either with sodium carbonate in a platinum crucible or with sodium peroxide in a nickel crucible and take water extract for the determination of vanadium.

Neutralize the solution with H_2SO_4 and make the solution approximately 0.5 N in sulphuric acid. Add 1 ml of 1:2 phosphoric acid and 0.5 ml sodium tungstate solution for each 10 ml of sample solution and cool. Take in a 100 ml. volumetric flask, dilute to the volume measure the absorbance of the solution at 400 nm against a reagent blank and determine the percentage of vanadium from the calibration curve prepared from the standard solution.

ZIRCONIUM ORES

Determination of Zirconium in Zircon & Eudialite

Zircon ores containing much silicon ore fused with Na_2CO_3 or a mixture of Na_2CO_3 and $Na_2B_40_7$ or KOH fusion in nickel crucible. Zirconium associated with rare earth element is first treated with concentrated sulphuric acid to dissolve rare earth element and zirconium remains as insoluble residue and is fused with flux as described above.

$$ZrSiO_4 + 2Na_2CO_3 = Na_2ZrO_3 + Na_2SiO_3 + 2CO_2$$

$$ZrSiO_4 + 3\ Na_2CO_3 + Na_2B40_7 = Na_2ZrO_3 + Na_2SiO_3 + 4NaBO_3 + 3CO_2$$

The melt is leached with conc. HCl to preclude hydrolysis of zirconium and separate silica by dehydrations and extract in concentrated HCl and water. Filter silica through Whatman 40.

Reagents:

1. **HCl Sp.Gr. 1.19, 2N**
2. **EDTA. 0.01 M & 0.05 M solutions**
3. **Eriochromeblack T, a mixture with NaCl (1:50)**

1 ml of 0.05 M EDTA solution = 4.56 mg. Of Zr.

Fuse a sample of zircon or eudialite containing 5-10 mg. of Zr. With a ten-fold of the flux in a pt. crucible, heat first on a burner to red heat then in a muffle furnace at 1000^oC for 15-30 mins. Add HCl, density 1.19, cover the crucible with a watch glass and heat on water bath. When CO_2 evolution stops remove the watch glass and evaporate the solution to dryness. Repeat the process 2 times and finally dissolve the salt.

Separate the ppt SiO_2 x H_2O on filter, wash with $2NH_4Cl$ and collect the filtrate and washings in 50 or 100 ml. volumetric flash. The acidity of the solution should be 2N. Add a small portion of eriochrome black T to the solution, boil for 7-10 minute until a persistent blue violet colour develops and titrate with a 0.01 M EDTA until the solution turns violet pink. Now heat the solution again and if blue violet colour is restored, continue the filteration with EDTA until the violet pink colour persists.

1 ml. of 0.01 M EDTA = 0.9122 mg. Zr.

Determination of Zirconium by Gravimetry

Principle

The mineral is decomposed by two successive fusions (sodium carbonate and potassium pyrosulphate). The zirconia is precipitated by hydrolysis with thiosulphate.

Reagents

1. **Anhydrous Na_2CO_3**
2. **$K_2Cr_2O_7$**
3. **H_2SO_4**
4. **HCl**
5. **$Na_2S_2O_3$**
6. **Dil .NH_3**
7. **Dil NH_4NO_2 soln.**

Procedure

Fuse 0.5 g of 300# zircon sample with 5 g of anhydrous sodium carbonate in a platinum crucible, first on a burner to red, heat then in a muffle furnace at 1000^oC for 15-20 mins. Cool the crucible and extract the mass in the hot water. Filter this through What man 40.Wash the residue with hot water. Preserve this filter ate A.

Ignite the residue to burn the paper in a platinum crucible. Fuse this with potassium pyrosulphate on burner. Cool the mass and extract in 10 ml dilute sulphuric acid and 50 ml water. Boil this for about 10 mins to dissolve zirconium completely. Filter this through What man 40 .Wash the residue with hot water. Preserve this filter ate, B.

Ignite the residue in platinum crucible. Fuse the mass with 3-4 g of anhydrous sodium carbonate. Cool the crucible and extract the mass in hot water. Filter this through What man 40 and collect the filterate with preserve filterate A and above C.

Ignite the residue above in platinum crucible to burn off the filter paper. Fuse this with potassium pyrosulphate. Cool and extract the mass in 10 ml dilute sulphuric acid and 50 ml water. Filter this through What man 40 and collect the filterate in filterate B and above D.

Determination of SiO_2

Acidify the aqueous extract C above with dilute hydrochloric acid. Evaporate this on a hot plate to dryness. Continue heating for about one hour to dehydrate the silica. Extract this with 5 ml dil. HCl and water. Filter this through What man 40 . Wash the residue with hot water. Ignite the residue in platinum crucible. Weigh the residue. Add 3-4 drops of dilute sulphuric acid and 15 ml 40 % hydrofluoric acid. Expel all acid on asbestos sheet. Finally, ignite the crucible to red heat. Cool and weigh the crucible. Calculate percentage loss and report it as SiO_2.

Fuse residue after silica with little potassium pyrosulphate and extract this in preserved filterate D above. Now make up the filterate to 250 ml.

Pipette out 50 ml aliquot from the above solution in a 250 ml beaker. Neutralize it with $NaHCO_3$. until a slight permanent precipitate is formed. Dissolve this by adding a few drops of dil.H_2SO_4..Boil till all CO_2 expels.

To this hot solution, add 10 g $Na_2S_2O_3.5H_2O$ dissolved in 20 ml of water. Continue boiling for an hour, replacing water lost by evaporation.

Add filter paper pulp. Filter through What man 41 filter paper. Wash the precipitate on the paper 15 times with hot water. The precipitate contains ZrO_2 (HfO_2) and some Al_2O_3 and TiO_2.Ignite it in a platinum crucible and report this as ZrO_2.Further refining can be done by digesting this crude ZrO_2 with HCl. Make this ammoniacal and again filter through What man 40.Wash the residue this time with dil.ammonium nitrate solution. Ignite the residue to constant weight and weigh as ZrO_2.

$$ZrO_2\% = \frac{\text{Weight of the } ZrO_2 \text{ x } 100 \text{ x dilution}}{\text{Weight of the sample taken}}$$

COAL AND GRAPHITE

Coal, graphite and diamond are the naturally occurring substance, which are mainly composed of carbon. They are entirely different from each other in physical look and physical properties. They are the allotropes of carbon. Coke is a by-product of destructive distillation of coal. Coal, coke and graphite is analysed for the chemical composition. On the other hand diamond is never subjected to chemical analysis but its grade is determined from physical properties.

An analytical chemist working in the field of minerals has to analyse coal, coke and some times graphite for confirming their grade. Therefore, the analysis of coal, coke and graphite is included here.

Analysis of coal, coke and graphite is divided into three parts namely proximate analysis, ultimate analysis and analysis of ash. Proximate analysis gives the rough grade of the coal whereas analysis of ash gives the analysis of combustion waste. Ultimate analysis and determination of calorific value gives a closer look on the grade of the coal.

In this Chapter, proximate analysis, analysis of ash and N, S, determinations are only included as the ultimate analysis and determination of calorific value needs special apparatus. Hence they are not included in this text.

A. Proximate Analysis:

1. Moisture: The common indirect method in which coal is heated for 60 minutes in an air oven at 105°C and the loss in weight is assumed to be the moisture is rather inaccurate even with high rank coal and the inaccuracy increase with decreasing rank. Use of current of nitrogen gives appreciably good determination of moisture. Hence, the moisture determination should always be carried in current of nitrogen.

Procedure: Weight 1 g. of coal sample in silica patty dish. Tap the crucible to spread the sample in uniform thin layer. Place the patty dish in an oven maintained at 105°C in current of nitrogen for 60 minutes. Cool the patty dish in desiccators and weigh. The loss in the weight is the quantity of moisture in the sample.

2. **Volatile Matter**: Loss in weight of the coal sample at 930 ± 20°C is reported as volatile matter. Volatile matter is composed of coal gas, gas ammonia, benzene, toluene, phenol and tar. Though these are combustible their heat energy is rarely utilized in any furnace and are driven off with waste gases or they burn at the mouth and the energy released is of little use.

Procedure: Weigh 1 g. of coal sample (preferably dried sample at 105°C) in volatile matter crucible. Tap the crucible to form a thin layer. Close all air inlet and outlet of the furnace. Add 2-3 drops of benzene in the crucible and place this in muffle furnace maintained at 930 ± 20°C for seven minutes. Cool the crucible in desiccators and weigh. The loss corresponds to the quantity of volatile matter and moisture if dried sample is not used. Correct the determination for moisture by multiplying the factor [100/(100 - % moisture)]

C. **Ash:** Spread 2 g of sample in silica patty dish. Place the patty dish in cold furnace at 500°C for 30 minutes and at 750±50°C for further 60 minutes. Cool the patty dish on metal for 5 minutes and cool finally to room temperature in desiccators and weigh. The weight of the un-burnt residue corresponds to the quantity of ash. Correct the determination for moisture (if un-dried sample is used) by multiplying the factor [100 / (100 - % of moisture)].

$$\% \text{ Ash} = \frac{\text{weight of ash} \times 100}{\text{wt. of the sample } (100 - \% \text{ of moisture})}$$

$$\text{Fixed Carbon } \% = 100 - (\% \text{ moisture} + \% \text{ VM} + \% \text{ Ash})$$

D. Determination of Sulphur in Coal (ESCHKA's Method)

One g of coal is intimately mixed with 3 g. of Eschka mixture consisting of 2 parts of porous, calcined magnesia and 1 part of anhydrous sodium carbonate. The mixture is taken in a platinum crucible and this is covered about 2 g more of Eschka mixture. Fuse the mass carefully a low flame, till all black particles burned out. Cool the crucible. Extract the mass in 100 ml. DM water in 250 ml. beaker by gradual heating on hot plate. Remove crucible and wash it carefully. Filter this through Whatman 40. Wash the residue 5-6 times with hot water. Add 10 ml. bromine water, acidify the filtrate with dilute hydrochloric acid. Boil this, add 20 ml, 10% Barium chloride solution to this. Boil for 30 minutes. Cool this for 3-4 hours preferably leave this overnight. Decant the water from the beaker without disturbing the precipitate. Finally filter the precipitate through Whatman 42 filter paper. Wash this 5-6 times with cold water. Ignite the filter paper along with the precipitate in platinum crucible at 800^{o}C. The carbon from the filter paper should be burned below 600^{o}C.

$$\% \text{ of S} = \frac{\text{Wt. of } BaSO_4 \text{ x } 0.1374 \text{ x } 100}{\text{Wt. of the sample}}$$

E. **Determination of Nitrogen (Kjeldahl method)**

Weigh accurately 0.1 to 0.2 g of the sample and 2 g. of catalyst (87 parts of K_2SO4 and 13 parts of $HgSO_4$) and transfer this into a Kjeldahl flask. Shake to mix, add 10 ml. concentrated sulphuric acid and shake. Place the flask on a hole in an asbestos board and incline the neck at an angle of 60^0. The hole must be such that it should cover the liquid. Heat gradually to boiling, continue boiling for 15 to 20 minutes, add small volume of concentrated sulphuric acid if required. Cool, carefully dilute with about 200 ml. of water, add few pieces of cracked porecelain to prevent from bumping and then add 25 ml. of solution containing 80 g of sodium thiosulphate or 40 g. of sodium or potassium sulphide per litre. Next add sufficient sodium hydroxide solution to make the solution strongly alkaline, add alkali solution very slowly from the side of the flask. Connect the condenser. Place other end of the condenser dipped in measured solution of standard sulphuric acid. Distill about 150-200 ml. into the standard sulphuric acid solution. Remove the dipped end of the condenser. Put off the flame, disconnect the flask, wash the condenser into the standard sulphuric acid. Add 2-3 drops of methyl red indicator. Titrate this against standard alkali solution. Find a blank for the standard sulphuric acid solution. Find the volume of acid consumed by the distilled ammonia. Estimate the quantity of nitrogen in the sample and the percentage of nitrogen in the sample.

1 ml, 0.5 N, $H_2SO_4 \equiv 0.007$ g of nitrogen.

F. **Analysis of Ash: Determination of SiO_2 & preparation of stock solution**

Fuse 1 g. of ash with 3-4 g. of sodium carbonate in platinum crucible. Cool, and extract the mass in dilute hydrochloric acid and water. Evaporate the solution on hot plate to dry. Bake this to dehydrate completely on hot plate for 30 minutes. Add 5 ml. concentrated hydrochloric acid and 50 ml. DM water, boil this, cool and filter this through Whatman 40. Wash the residue 5-6 times with hot water. Preserve the filtrate for further determinations. Transfer the residue along with filter paper to a platinum crucible. Heat this in muffle furnace at 1000^{o}C. Cool, and weigh the mass. Add 2-3 drops of dilute sulphuric acid and 10-15 of 48% hydrofluoric acid. Heat this on asbestos sheet to fumes. Expel all fumes from the crucible. Now heat crucible on a low burner initially and finally at 1000^{o}C in a furnace. Cool, and weigh the residue. The loss corresponds to the quantity of silica in the ash. Fuse the mass left, after hydrofluorisation, in the crucible with potassium pyrosulphate. Extract this in the filtrate preserved for further analysis. Make up the filtrate to 250 ml. in volumetric flask. Follow the procedures given in the chapter on determination of major and minor constituent from the stock solution.

CEMENT

Portland cement is mainly composed of tricalcium silicate along with dicalcium silicate, mono calcium silicate, calcium aluminate also small amount of iron and little calcium sulphate (acting as a retarder). Cement is analysed for SiO_2, Fe_2O_3, Al_2O_3, CaO, MgO, SO_3, Loss on Ignition, Na_2O, K_2O on routine basis and also P_2O_5, MnO_2, TiO_2 free CaO at regular interval.

Determination of Silica and preparation of stock solution:

Weigh 1 g. of cement sample in 250 ml. beaker. Add 25 ml. concentrated hydrochloric acid and 5 ml. concentrated nitric acid. Digest this on hot plate. Expel all acid. Dry, dehydrate and bake silica for 30 minutes at 115-120°C. Wet the mass with 5 ml. concentrated hydrochloric acid and 50 ml. DM water. Boil this & cool. Filter this through Whatman 40 filter paper. Wash the residue 5-6 times with hot water. Preserve the filtrate for determination of other radicals. Transfer the residue along with filter paper to a platinum crucible. Ignite this at 1000°C. Cool, and weigh the mass. Add 2-3 drops of dilute sulphuric acid and 10-15 ml. of 48% hydrofluoric acid. Heat this on asbestos sheet slowly to expel all acid. Heat the crucible on low flame initially and finally to blast flame at 1000°C. Cool this in desiccators and weigh. The loss corresponds to the quantity of silica in the sample.

$$\% \ SiO_2 = \frac{\text{loss of wt. x 100}}{\text{wt. of sample}}$$

Fuse the residue left after hydrofluorisation with small amount of potassium pyrosulphate. Extract this in the filtrate preserved for other radicals. Make up the filtrate to 250 ml. Follow the procedure given in the chapter on determination of major and minor constituents from the stock solution.

1.3 DETERMINATION OF CALCIUM FLUORIDE IN FLUORSPAR SAMPLES BY CHEMICAL PHASE TECHNIQUE.

Scope

The method is suitable for determination calcium fluoride in fluorspar sample in the range from 0.30 to 96.00% CaF_2.

Principle

Finely powdered (-150 mesh) fluorspar sample is digested with 8% aluminium chloride solution in 0.1 N hydrochloric acid, the loss in weight corresponds to calcium fluoride (CaF_2) after appropriate corrections due for all acid soluble contents of sample.

Reagents and equipments

All the reagents used were of analytical grade.

1. **Hydrochloric acid, 0.1 N**
2. **Acetic acid, 10% (V/V)**
3. **Aluminium chloride, 8%** - Dissolve 80 g Ar anhydrous aluminium chloride in one litre ice cold 0.1 N hydrochloric acid. Cool to room temperature, filter by Whatman filter paper No.40 and keep in a glass bottle.
4. **Platinum crucibles, 25 ml capacity**
5. **Muffle furnace, Temp.-1000°C range.**
6. **Electric oven, Temp. 280°C.**

Procedure

(A)

- Accurately weigh 0.5000 g fluorspar sample (-150 mesh) and transfer to a 250 ml beaker.
- Add 25 ml aluminium chloride solution
- Stir with a glass rod.
- Digest on a steam bath for 1 hr.
- Filter the sample through Whatman filter paper No.40. Quantitatively transfer the residue to filter paper (Use policeman)
- Wash the residue with hot water (8-10 washings)
- Transfer filter paper and residue into a tared platinum crucible.
- Transfer platinum crucible to a cold furnace and ignite filter paper at $500^{o} \pm 10^{o}$C. Give 1 hour soaking time.
- Cool crucible to room temperature in an efficient desicator and weigh.
- The % loss in weigh of sample corresponds to calcium fluoride and other acid soluble matter of sample, viz. carbonates, ferruginous matter, etc.

$$\text{\% loss in weight (A)} = \frac{\text{Weight of sample} - \text{Weight of residue} \times 100}{\text{Weight of sample}}$$

(B) Correction for acid – soluble matter.

- Treat 0.5000 gm finely powdered sample taken in (a) with 25 ml. 10% acetic acid solution in a beaker
- Digest the sample on steam bath for 1 hr.
- Filter the residue through Whatman filter paper No.40. Wash 8-10 times with hot water.
- Ignite the filter paper with residue, starting from a cold furnace to 550 ± 10^{o}C.
- Calculate acid soluble matter from the loss in the weight of sample after treatment.

$$\%\ \text{Acid Soluble matter (B)} = \frac{\text{Weight of sample} - \text{Weight of residue} \times 100}{\text{Sample weight}}$$

(C) **Calculation of % CaF_2 in sample:**

Deduct the % acid soluble matter (B) from the percent loss in weight (A), the difference corresponds to % CaF_2 dissolved in aluminium chloride solution by forming $CaCl_2$ and AlF_6^{3-} compounds

% CaF_2= % Loss in weigh of sample (A) - % Acid soluble matter of sample (B)

EXPERIMENTAL

All the reagents used were analytical grade.

Reagents

(a) **0.1 N hydrochloric acid** – Dilute 100 ml 1N hydrochloric acid to 1 litre with water.

(b) **10% Acetic acid** – Dilute 100 ml glacial acetic acid to 1 litre by water

(c) **Aluminium chloride reagents:** Dissolve 80 grams analytical grade anhydrous aluminium chloride in 1 litre ice cold 1N hydrochloric acid. Cool to the room temperature and filter through Whatman filter paper No.40. Preserve in a glass bottle.

Procedure:

(a) Weight 0.5000 g sample and transfer to a 250 ml. corning beaker. Add 25 ml aluminium chloride reagents. Digest on a steam bath for one hour. Filter through sinter glass G-4 crucible. Wash the residue with hot water for 6-7 times. Dry the residue at 180°C in an electric oven for one hour. Cool it to room temperature in a desicator and weight it. Alternately, filter the residue through Whatman filter paper No.40, wash it thoroughly with hot water. Ignite and residue and paper in a platinum crucible at 550 ± 10°C in a furnace for 15 minutes. Cool it to room temperature and weigh it.

The % loss in weight corresponds to CaF_2 and other acid soluble matter in sample, such as carbonates, ferruginous material, etc.

(b) Correction for acid soluble matter : Treat 0.5000 a sample with 25 ml with 10% acetic acid or 0.1 N hydrochloric acid in a 250 ml beaker. Digest the sample on steam bath for one hour. Filter it through tarred sinter glass G-4 crucible. Dry the residue at 180°C and weigh it after cooling to room temperature. Calcuate % loss in weight, which is the acid soluble matter. Alternately, filter the residue through Whatman filter paper No.40, wash 6-7 times with hot water, ignite the residue at 550 ± 10°C and calculate acid soluble matter. Deduct the percent acid soluble matter from the percent aluminium chloride soluble sample the difference is % CaF_2.

1.4 CHEMICAL QUALITY EVALUATION AND STANDARDIZATION OF SODIUM OLEATE FOR APPLICATION AS FROTH FLOTATION REAGENT.

Scope

The chemical analysis methods are standardized to determine moisture, pH, total alkalinily, matter soluble in ethylalcohol, Free alkali, free acid, total fatty acid, free fatty matter, unsaponi fible matter, unsapanified matter, iodine number and bromine number.

Introduction

Sodium oleate has been a wellknown anionic collector employed in froth flotation beneficiation. It is a saponified product of oleic acid – along chain fatty acid with one double bond at 9 – carbon position. The performance of sodium oleate depends on the quality of mother oleic acid and impurities present there in. Hence, it is imperative to evaluate and standardize the quality of commercial sodium oleate to ensure its optimum performance in froth flotation tests.

Methodology

Moisture

Dry 10 to 15 gms. of homogeneous soap sample in a weighed corning glass petri dish on a steam bath to constant weight to third decimal. Keep dried sample in desicator over fleshly heated silica gel. This dried material has been used for all determination.

Note : This estimation gives loss of moisture and other volatiles at 100^{o}C.

pH of Soap solution

Dissolve 5 gms. of dried soap sample in 100 ml. Distilled water on steam bath. Cool it to room temperature and measure pH using a pH meter calibrated and equilibrated suitably in the pH range 0-14 pH meter. Report as pH of 5% aqueous solution.

Note : **(i)** Calibration and setting of the pH meter may be carried out according to the instrument operation manual. (ii) The pH of 5% solution usually falls in 8.5 to 9.5 range.

Total alkalinity of soap

Dissolve 5 grams of dried soap material in 100 ml distilled water by heating over low flame of burner. Filter it through Whatman filter paper no. 40, wash it thoroughly with hot water until the filter paper is free from soap. Titrate the filtrate in the cold to the methyl orange end point with 0.1 N hydrochloric acid. Report percent total alkalinity as sodium oxide.

Calculation

$$\text{\% Total alkalinity as } Na_2O = \frac{\text{Titration in ml x normality x 0.031 x 100}}{\text{Weight of soap}}$$

Matter soluble in ethyl alcohol

Soap is soluble in ethylalcohol. Added builder such as carbonates, borates, silicates, phosphates and other contaminants are insoluble.

Procedure

Put 2 to 5 grams of the dried soap sample into a covered beaker and add 200 ml of absolute ethyl alcohol and digest it on a steam bath for two hours. Filter through a weighed lG – 4 sinter glass crucible under mild suction in a clean area free from carbon dioxide and other acid fumes. Wash the residue with warm absolute ethyl alcohol until it is free from soap – usually six to eight perfect washings are sufficient. Reserve the filtrate and washings for estimation of free alkali/free acid. Dry the residue by heating sinter glass crucible at 100°C for one hour in an oven. Cool and weight the total matter insoluble in alcohol. Calculate matter soluble in ethyl alcohol.

Free alkali/Free acid in soap

Heat the clear filtrate reserved from the ethyl alcohol soluble matter to incipient boiling and add 0.5 ml. of one percent phenolphthalein indicator. If the colour of the solution is pink, hints the presence of free alkali, titrate from pink to colourless end point with 0.10 N hydrochloric acid. Calculate free alkali present. If, the reaction of the alcoholic solution of soap with phenolphthalein is acidic, titrate it with 0.10 N sodium hydroxide to pink end point. Calculate free acid as oleic.

Calculation

(i) $$\text{\% Free alkali as sodium hydroxide} = \frac{\text{Titration ml x Normality of acid x 0.040 x 100}}{\text{Weight of soap}}$$

The free alkali is also expressed as sodium oxide or sodium carbonate with the factor 0.031 or 0.053 respectively.

(ii) $$\text{\% Free alkali as sodium hydroxide} = \frac{\text{Titration mlxNormality of acid x 0.02825 x 100}}{\text{Weight of soap}}$$

Total fatty matter (TFM)

Transfer 2 to 5 grams of dried soap sample to 250 ml covered beaker. Add 150 ml. distilled water to the sample and dilute nitric acid until slightly acidic, heat on a steam bath for one hour. The fatty matter collects on the top and the solution below appears perfectly clear. Cool to the room temperature in ice water. Transfer the liberated fatty matter along with the solution and 50 ml chloroform to a 500 ml separatory funnel. Shake it for one minute, let the two layers separate and transfer the lower chloroform extract to a beaker. Again, similarly extract the fatty matter in solution with 25 ml of chloroform for two to three times and transfer it to the beaker. Then transfer the whole chloroform extract to a 200 ml separatory funnel, rinse the beaker with chloroform. Wash the chloroform extract with 25 ml of water for two to three times. Now transfer the chloroform extract to a weighed 100 ml beaker. Evaporate off the chloroform on a steam bath and dry on it for 30 minutes. Cool in a desicator and weigh as total fatty matter.

Calculation

$$\% \text{ TFM} = \frac{\text{Weight of fatty matter x 100}}{\text{Weight of soap}}$$

Free fatty matter (unsaponified and unsaponifiable matter – FFM)

Take 2 to 5 grams of the dried soap in a 250 conical flask and add 0.1 to 0.2 gram of sodium bicarbonate. Dissolve sample in 100 ml of 50% ethyl alcohol. Warm on a steam bath to dissolve it. Filter it through Whatman filter paper No.40 and wash the filter thoroughly with 50% ethylalcohol and a little petroleum ether (60-80 ^{o}C). Shake it vigorously for one minute. Let the two clear layers separate and then draw off upper petroleum ether layer into another 250 ml separatory funnel. Repeat the above extraction for 2-3 times with 25 ml portion of petroleum ether. Wash petroleum ether fraction in separatory funnel with 0.1 N sodium hydroxide and ethylalcohol mixture (one to one by volume) for two to three times. Evaporate the petroleum ether in a weighed beaker on a steam bath and dry the residue on steam bath for 30 minutes. Weight of the residue corresponds to free fatty matters**.**

Calculation

$$\% \text{ FFM} = \frac{\text{Total weight of residue x 100}}{\text{Weight of soap}}$$

Unsaponifiable matter

Put 2 to 5 grams of dried soap in a 250 ml. beaker. Add 30 ml of ethylalcohol and 5 ml of 50% potassium hydroxide solution and then heat it on a steam bath for two hours and then boil over a low flame of burner for 15 minutes. Transfer the solution to a 250 ml separatory funnel, add 20 ml ethyalcohol and 80 ml of distilled water. Mix it well. Now add 50 ml petroleum ether (60-80^{o}C) and shake vigorously for 30 seconds. Allow the two layers to separate perfectly clear. Draw upper petroleum ether layer in another separatory funnel. Continue extraction with fresh 25 ml portion of petroleum ether for three to four times and collect all extraction fractions in the separatory funnel. Wash the petroleum ether extract with ethylalcohol water mixture (1:5 by volume) until the washing is just acidic or neutral to the methylorange indicator. Transfer petroleum ether layer to a weighed beaker and evaporate on a steam bath and then dry the residue for 30 minutes. Cool and weigh it corresponds to unsaponifiable matter.

Calculation

$$\text{\% Unsaponifiable matter} = \frac{\text{Weight of residue x 100}}{\text{Weight of soap}}$$

Unsaponified matter

The unsaponified matter is computed by deducting the percent of unsaponifiable matter from the percent of unsaponified and unsaponifiable matter (FFM).

Examination of fatty matter for unsaturation – Determination of iodine number and bromine number

The total fatty matter separated from soap has been employed as sample for estimation of iodine number and bromine number. In iodine number the total iodine consumed by the sample is estimated which may be either the addition at a double bond or the substitution on the chain. While in bromine number a less common determination, envisages the correction for any substitution and hence only demonstrate the degree of unsaturation. However, both the methods have been used.

(i) Iodine number – Wijs method

Weigh 0.1 to 0.2 grams of fatty matter into an iodine conical flask. Dissolve it by mixing in 25 ml of chloroform. Now add from a pipette 245 ml of wijs iodine solution or standard iodine monochloride solution. Just moisten the stopper with 15% potassium iodide solution and let stand the flask in dark closed for one hour at room temperature. The above steps can be conducted in a 500 ml conical flask nicely cover with a watch glass or a glass stopper. After one hour add 20 ml of 15% potassium iodide solution and 100 ml of distilled water, boiled and cooled. Titrate it immediately with 0.10 N sodium thiosulphate solution to disappearance of blue colour of starch indicator. Run blank of wijs solution.

Calculation

$$\text{Iodine value (Iodine number)} = \frac{\text{ml. of thiosulphate consumed by sample x normality of thiosulphate x 12.629}}{\text{Weight of sample}}$$

The iodine number represents the number of centigrams of iodine absorbed by 1 gram of fatty matter, i.e. the percent of iodine absorbed.

Note : Wijs solution : Dissolve 13 gms of pure analytical grade iodine in 1 litre of in 1 litre of analytical grade acetic acid. Titrate 25 ml with 0.10 N sodium thiosulphate using potassium iodide and starch. Put aside about 10 ml of iodine solution and in the rest of the solution pass pure chlorine gas until the red colour of the solution just turns to the yellow colour and the original sodium thiosulphate titration just doubled. Then add the original solution to neutralize any free chlorine. Preserve in amber-coloured bottle and use only in one month period.

Bromine value

Take 0.1 to 0.2 grams of fatty matter in a 250 ml iodine flask or alternately to a 500 ml. conical flask. Dissolve fatty matter in 25 ml of carbontetra-chloride. Pipette 25 ml of 0.33 N bromine reagent into the flask containing the sample. Put the stopper and let it stand for two minutes at room temperature. The immerse the flask in ice water and quickly add 30 ml of 25 percent potassium iodide solution. Restopper and shake the solution to absorb vapors of bromine and then wash down the walls of flask with distilled water. Add 75 ml of 10 percent sodium chloride solution to overcome emulsification of the solvent. Titrate the iodine liberated with 0.10 N sodium thiosulphate solution to disappearance of blue colour of starch indicator. Run a blank. The difference in litre value for blank and residual free bromine is the measure of percent total bromine absorbed.

When the end point for total bromine absorbed reached and recorded add 5 ml of potassium iodate solution the hydrobromic acid liberated from substitution reaction is transformed into the equivalent free iodine. Mix well and titrate liberated iodine with 0.10 N hyposolution. The difference of milliliters of hypo solution consumed for liberated hydrobromic acid and blank is the bromine substitution value. The difference of the percent total bromine absorbed and bromine substitution value is reported as bromine addition value.

Calculation

(i) Bromine substitution

$$= \frac{\text{(Ml. of hypo equivalent to liberated hydrobromic acid-Blank)} \times \text{Normality of hypo} \times 0.0799 \times 100}{\text{Weight of sample}}$$

(ii) Percent total

$$= \frac{\text{(Blank-ml. of hypo equivalent to residual free bromic acid)} \times \text{Normality of hypo} \times 0.0799 \times 100}{\text{Weight of sample}}$$

(iii) Bromine addition value = Percent total bromine absorbed – (2 x bromine substitution value)

Note

(A) Bromine reagent (0.33 N) – Dilute 26.6 gms of bromine to one litre with carbon tetrachloride.

(B) Potassium iodate solution – Dissolve 21.4 gms of potassium iodate in one litre distilled water.

1.5 SPECTROMETRIC (COLOURIMETRIC)METHODS OF ANALYSIS

General Consideration

The technique is based on the fact that when visible (380-800 nm), ultraviolet (200-400 nm), etc. electromagnetic radiations passes through a colour solution, the quantity of light absorbed (or transmitted) varies depending upon the concentration of the colour component (absorbing species) of the solution. The intensity of the colour of the unknown is compared against a solution of known concentration by following the same procedure and the concentration/percentage of the colour component present in the sample is determined.

Law of the absorption of light

The colourimetric analysis is based upon Lambert and Beer's law :

(i) Lambert Law: When mono-chromatic light passes through a transparent medium, the rate of decrease in intensity with the thickness of medium is proportional to the intensity of the light or that the intensity of the emitted light decreases exponentially as the thickness of the absorbing medium increases arithmetically.

Thus, the law by Briggsian logarithm :

$$It = Io\ 10^{-k.t}$$

Where Io is the intensity of the incident light, it is the thickness of the medium. It is the intensity of the transmitted light, and K is extinction coefficient.

(ii) Beer's law: The intensity of a beam of monochromatic light decreases exponentially as the concentration of the absorbing medium increases arithmetically.

Thus,

$$It = Io.\ 10^{-k'c}$$

Where C is concentration and K' is a constant. These two laws are combined to obtain following exponential form:

$$It = Io.\ 10^{E.C.t.}$$

$$\text{Or } \log \frac{Io}{It} = E.C.t. = A \text{ (absorbance)}$$

Where E is molar extinction coefficient.

This is the fundamental equation of colourimetry and termed as Lambert-Beer Law.

The concentration of an unknown solution can be calculated knowing A,E,t provided the Lambert = Beer law is applicable.

$$C = \frac{\log Io/It}{E.t.} = \frac{A}{E.t.}$$

If a coloured system does not show conformity to Lambert Beer Law, a standard calibration graph is prepared by plotting other transmittance or absorbance value (ordinate0 against concentration using a series of standard solution. From this graph, concentration of unknown solution can be computed corresponding to its absorbance reading. An identical procedure must be followed in preparing the coloured solution of unknown sample and the standard colour solution. However, a calibration graph is applicable to specific instrument only.

Instrumentation

Absorption measurements are made with various instruments, i.e. colourimeter, photoelectric colourimeter, and spectrophotometer which are constructed according to the following scheme

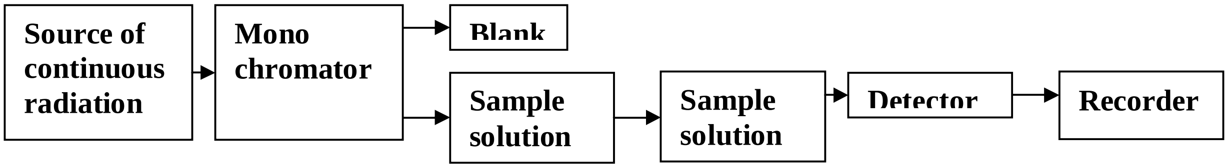

Table- Photometric analytical method

Method	Region of spectrum	Monochromator	Technique of recording of light absorption (Detector)
Colourimetry	Visible	Absent	Visual
Photoelectric colourimetry	Visible	Colour filters	PMT
Spectrophotometry	Visible Ultraviolet	Diffraction grating Prism	PMT

Operation

In using a single beam spectrophotometer, the wavelength set to the absorption maximum of the analyte to be determined. The instrument is adjusted to red zero transmittance when no light passes to detector. The reagent blank is then positioned into the light path and adjust the read out to a 100 percent transmittance or zero absorbance setting. The light is then passed through the sample to obtain the absorbance or transmittance and related to concentration either through the use of calibration graph or by the use of algebriae method.

$$\frac{W_1}{A_1} \times \frac{A_2}{W_2} \times 100 = \% \text{ concentration}$$

A_1 = Absorbance of standard solution
W_1 = Weight of standard (in mg or gm)
A_2 = Absorbance of the sample
W_2 = Weight of sample taken (in mg or gm)

In a double beam spectrophotometer, a monochromatic light beam is split into two components. The instrument is adjusted to zero by placing reagent blank in both the component beam after wavelength setting to the absorption maximum. Then one of the reagent blank is replaced by sample solution (absorbing solution) and the difference of absorbance between the two is determined simultaneously. This absorbance value is used for calculating percent analyte in solution.

Method

i. Tungsten:

Principle

Tungsten is preferentially extracted in tartaric acid solution after fusion with potassium pyrosulphate. The W^{VI} is reduced to W^{V} by stannous chloride in strongly acidic medium followed by reaction of thiocyanate ion to form a W^{V} green-yellow complex, which absorbs at 400 nm.

Reagents

- **(i)** **Standard Tungsten solution:** Dissolve 1.7940 g. of reagent grade Na_2WO_4. $2H_2O$ in water. Add one pellet of sodiumhydroxide dissolve and dilute to one litre. 1 ml -= 1 mg of tungsten with a pipette, transfer 10 ml of this stock solution to a 100 ml volumetric flask and dilute to the mark. 1 ml = 0.10 mg of tungsten.
- **(ii)** **Stannous chloride 2M**: Dissolve 113 g stannous chloride dihydrate in concentrated hydrochloric acid. Make volume to 250 ml with concentrated hydrochloric acid.
- **(iii)** **Tartaric acid** : 7.5% **-** Dissolve 7.50 gm of tartaric acid in 100 ml water**.**
- **(iv)** **Potassium thiocyanate** – 20% **-** Dissolve 20 gm of potassium thiocyanate in 100 ml water.

Procedure

- Transfer 0.10 – 0.40 g sample in dry test tube and mix with five fold of potassium pyrosulphate.
- Fuse over a burner and keep it red hot for 10-15 minutes.
- Spread melt over the walls of test tube and allow it to cool.
- Add 10-15 ml of tartaric acid solution in the test and put a glass rod.
- Heat the tube gently in a hot water bath until the cake breaks up.
- Remove the test tube from water bath and filter solution in 100 ml. Volumetric flask using Whatman No.40 filter paper, wash tube and residue with 1% hot tartaric acid solution. Usually five to six washings are sufficient.
- To the filtrate, add 10 ml of concentrated sulphuric acid, 20 ml of concentrated hydrochloric acid, and 5 ml of stannous chloride solution in that order.
- Mix well and digest on a steam bath for 10 minutes.
- Remove from heat and immediately chill in an ice bath to 10°C or less (minimum time should be given at this point) and then quickly add 10 ml of potassium thiocyanate solution, dilute to the mark and mix well. Return to the ice bath for 5 to 10 minutes.
- Remove the flask from ice bath and allow it to stand at room temperature for 10 minutes (The colour is stable for at least one hour).

- Measure the absorbance in a spectrophotometer at 400 nm using reagent blank for a null.
- Compute tungsten concentration from calibration graph.

Standard absorption concentration graphs Transfer 1,2,5,7,10,15 and 20 ml of 0.10 mg tungsten per ml stock solution to 100 ml volumetric flasks. The aliquots represent 0.10, 0.20, 0.50, 0.70, 1.00, 1.50 and 2.00 mg of tungsten respectively. Dilute to 25 ml and follow steps 5-12 plot the absorbance versus mg of tungsten on co-ordinate paper.

ii. Silica

Principle

A yellow coloured 12-molybdo-silicic acid forms reaction of silicate ion with molybdate ion in pH range of 1.6-4.90. The heteropoly blue of silicon is produced by the reduction of the molybdenum (vi) in the 12-molybdosilicic acid to the molybdenum (v) State. The intensity of the blue colour is measured at 650 nm.

Reagents

(i) **Standard silica solution –** Fuse 2.1393 g SiO_2 with 4.60 gm anhydrous sodium carbonate, maintaining melt for 15 minutes in platinum crucible dissolve in water, and dilute to 1 litre 1 mg SiO_2 per ml.
(ii) **Standard silica 0.1 mg SiO_2/ml** : Dilute 10 ml of 1 mg SiO_2/ml solution to 100 ml by water, store in polythene bottle.
(iii) **Ammonium molybdate solution, 5%** - Dissolve 5 g ammonium molybdate in warm water (60^aC) and make volume 100 ml.
(iv) **Oxalic acid, 8%** - Dissolve 8.00 g of oxalic acid in 100 ml of water.
(v) **Ascorbic acid, 5%** - Dissolve 5.00 g of ascorbic acid in 100 ml of water

Procedure

- Transfer 2.5 ml aliquot of 19 sample solution in 250 ml volume obtained in decomposition of silicates by sodium carbonate fusion, after usual separation of silica (SiO_2) by dehydration and baking and dehydrofluorisation.
- Add 20 ml distilled water and mix.
- Then neutralize acid by adding dilute sodium hydroxide solution using pH paper externally.
- Now add 0.40 ml dilute hydrochloric acid (1:1) to bring pH of solution around 2.2.
- To this add 5 ml of ammonium molybdate solution mix well and stand for10 minutes.
- Then add 10 ml of oxalic acid solution. Mix well by swirling, and add immediately 2 ml of ascorbic acid solution and again mix.
- Dilute solution to 100 ml by water and keep aside for 30 minutes at room temperature.

- Measure absorbance of the blue complex at 650 nm.
- Run a reagent blank.
- Calculate SiO_2 percentage using calibration graph**.**

Standard calibration graph – Transfer 0, 0.5, 1.0, 1.5, 2.0, 2.5, 3, 4 and 5 ml of the 0.1 mg SiO_2 per ml stock solution to 100 ml volumetric flask, dilute to about 20 ml by water and follow steps 3-18. Plot absorbance values versus mg silica per ml and use this graph for calculation of percent SiO_2 in unknown solution.

iii. Molybdenum in tungsten mineral

Principle

Thiocyanate ion react with Mo(V) in an acid solution to form coloured complex the maximum absorbance is read at 540 nm. The interfering effect of tungsten is overcome by adding tartaric acid which percents then formation of its thiocyanate complex**.**

Reagents

(i) **Molybdenum Standard solution,** 1 ml equivalent to 0.1 mg of molybdenum. Dissolve 2.0425 g ammonium molybdate in water dilute to 1 litre volumes Mo = 1 mg/ml. Dilute 10 ml of above solution to 100 ml to prepare 0.1 mg Mo/ml solution.
(ii) **Dilute sulphuric acid 1:1 and 1:4**
(iii) **Tartaric acid 10% :** Dissolve 10 g of tartaric acid in 100 ml water.
(iv) **Stannous chloride** : **35%** - Dissolve 350 g of $SnCl_2 – 2H_2O$ in 100 ml of concentrated hydrochloric acid by heating, dilute the clear solution with 900 ml water and add a few pieces of tin metal.
(v) **Ferric sulphate, 8% -** Dissolve 8 gm of ferric sulphate in 100 ml of N sulphuric acid.
(vi) **Potassium thiocyanate, 5%** - Dissolve 5 gm of potassium thiocyanate in 100 ml water (freshly prepared).
(vii) **Butyl acetate** : The extracting solution is prepared by shaking 250 ml of butyl acetate in a separating funnel with 5 ml of 5% potassium thiocyanate solution and 25 ml of 25% solution of stannous chloride. The solutions are allowed to settle and the aqueous solution is drawn off and discarded. The extracting solution deteriorates and must be prepared every 24 hours.

Procedure

Decomposition : Mix 0.1 – 0.5 g of mineral with a five fold quantity of sodium carbonate and fuse it over the flame, leach the melt with 50 ml of hot water, separate the residue on a What man No.40 filter paper, wash with 25-50 ml of 1% sodium carbonate solution and neutralize the filtrate with hydrochloric acid using pH paper externally. Add 10 ml of the acid in excess and make to 250 ml volume for taking aliquot.

Alternately the sample can be decomposed by treating 0.1 g of sample (Mo ~ 0.5%) with dilute perchloric acid (1:1), warm until the sample has dissolved. Heat to boiling, cover and fume. Cool somewhat and add 25 ml of water, boil a few minutes to expel free chlorine filter and use aliquot.

- Transfer appropriate aliquot to a 250 ml separatory funnel.
- Add 25 ml of dilute sulphuric acid (1:1) and mix.
- Now add 3 ml of ferric sulphate solution and shake for 30 seconds.
- Then add 5 ml of tartaric acid solution and shake for 30 seconds.
- Now add 10 ml of potassium thiocyanate solution and shake for 11 minutes.
- Add 10 ml of stannous chloride solution and shake vigorously for one minute.
- Add 20 ml of butylacetate from a pipette, stopper and shake for one minute.
- Allow the funnel and contents to cool and repeat the shaking.
- Allow the layers to separate and draw off and discard the lower acid layer.
- Add 50 ml of dilute sulphuric acid (1/1), 10 ml of potassium thocyanate solution and 5 ml of stannous chloride solution and shake well.
- Allow the layers to separate and draw off and discard lower acid layer.
- Transfer the butylacetate layer to a volumetric flask and stopper.
- Take butylacetate extract in an absorption cell and measure absorbance at 540 nm using a blank run to set the zero. Compute percentage of molybdenum from calibration curve. (The absorption maxima of the molybdenum thiocyanate complex is ~ 470 nm, but the measurement is made at a longer wavelength to avoid interference by tungsten).

Standard curve

Transfer 3 ml of ferric sulphate solution and 25 ml of dilute sulphuric acid (1:1) to separatory funnel and add 0.5, 1.0, 2.0, 4.0 and 5.0 ml of the 0.1 mg/ml molybdenum standard solution into each funnel, respectively and proceed as in steps 4 to 12. Construct a standard curve plotting absorbance against mg of molybdenum.

iv. Bismuth in polymetallic ore

Principle

Yellow bismuth diethyl dithiocarbonate is extracted over 9-11 pH in chloform. The formation of the diethyl dithiocarbonates of metals such as iron (iii), mercury, silver and copper is prevented by the use of an ammonical solution in the presence of cyanide and disodium enthylene diamine tetra acetate. The absorption maximum of the yellow complex is 400 nm.

Reagents

1. **Bismuth Standard** : 1000 mg of Bi per ml : Dissolve 1.0 gm of bismuth metal in 8 ml of 10 N nitric acid, boil gently to expel brown fumes and dilute

to one liter. Bismuth standard 10 ppm. Dilute 1 ml of the 1000 ppm Bi/ solution to 100 ml with water containing 5 ml concentrate nitric acid.

2 **Potassium bisulphate fused powder**

3. **Ethylene diamine tetracetic acid, disodium salt**

4. **pH paper range 5-12**

5. **Sodium diethyl dithiocarbonate solution 1%** - Dissolve 1.0 g sodium diethyl dithiocarbonate in 100 ml of water.

6. **Chloroform**

Procedure

Decomposition of Sample : Dissolve 1.00 – 5.00 gm sample in a mixture of 3 parts of concentrate nitric acid and 1 part of concentrated hydrochloric acid. Evaporate to dryness, bake and take up with 1:10 hydrochloric acid. Dilute to a known volume for the use of aliquots.

For siliceous samples or tailings, the sample is decomposed by fusion with potassium bisulphate or potassium pyrosulphate. Bring sulphates in solution by boiling fused cake with 2 ml nitric acid and 8 ml water.

- Take aliquot equivalent to 0.50 gm.
- Add water to make volume around 20-50 ml.
- Add 1 gm of ethylene diamine tetraacetic acid disodium salt and mix well to get clear solution.
- Add ammonia solution drop wise until the pH of the solution is between 5 and 6 using a pH test paper externally.
- Add 5 ml of sodium cyanide solution (5% aqueous solution), mix well and filter through a Whatman No.40 filter paper into a 250 ml separatory funnel.
- Add 1 ml of ammonia to the filtrate and mix.
- Add 1 ml of sodium diethyl dithiocarbonate solution and shake.
- Add 5 ml of chloroform and shake the stoppered separatory funnel for one minute.
- Place a plug of cotton in the steam of the funnel and transfer organic phase to an absorption cell.
- Read absorbance at 400 nm.
- Compute bismuth concentration using standard calibration curve.

Standard Calibration curve : To five separatory funnels each containing 8 ml of water and 1 gm of EDTA add respectively, 10, 20, 40, 60 and 80 mg of bismuth per ml using the standard solution containing 10 mg of bismuth per ml. Continue as described in steps 4-10. Construct a calibration curve using absorbance and mg of bismuth.

v. Determination of Fluorine in water sample

Principle

The method is based on decolorisation of zirconium-alizarin dye by fluoride ions. Colourless ZrF^{2-}_6 is formed in this reaction. With progressive increase in fluoride ion concentration, the colour changes from pink-yellow to bright yellow. Maximum absorbance is at 520 nm.

Reagents

(i) **Standard fluoride solution :** Dissolve 0.221 gm of NaF in 1 litre distilled water. 100 mg of fluorine per ml.

(ii) **Acid Zirconylalizarin reagent (Sauchi's method).** To 0.30 g zirconium oxychloride octathydrate or 0.25 g zirconium nitrate octahydrate, dissolved in 50 ml water, add 50 ml alizariureds water solution containing 0.07 g of the dye with swirling. To above solution add 900 ml acid mixture, prepared by mixing 1123 ml concentrated hydrochloric acid diluted to 500 ml and 37 ml concentrated sulphuric acid diluted to 500 ml.

Procedure

- Take 50 ml clear water sample in 100 ml volumetric flask.
- Add 10 ml zirconium alizarin reagent. Mix the solution well.
- Make volume to the mark using water sample.
- Wait for one hour and then compare colour with standards or read absorbance at 520 nm.
- Calculate fluoride concentration from calibration curve.

Calibration curve : Transfer 0.5, 1.0, 1.5, 2.0, 3.0, 4.0 and 5 ml of 100 mg fluorine per ml stock solution to 100 ml volumetric flask containing 25 ml deionized water and then follow steps 2-4 under procedure. Plot absorbance against mg of fluorine. A graph of inverse slope is obtained. A standard graph must be prepared each time a fresh batch of zirconium alizarin reagent is prepared.

vi. Antimony

Principle

Antimony (V), in a medium of 1 M hydrochloric acid, forms red-violet coloured complex with rhodamin-B dye. Absorbance of the red-violet coloured complex is measured at 550 nm. Antimony (V) is preferentially extracted in isopropylether to overcome interference of other cations in sample.

Reagents

1. **1 M hydrochloric acid**
2. **6 M hydrochloric acid**
3. **Aquous hydroxylamine hydrochloride 1%** - Dissolve 1 gm of $NH_2OH.HCl$ in 100 ml water.
4. **Acidic hydroxylamine hydrochloride 1%** - Dissolve 1 gm of $NH_2OH.HCl$ in 100 ml 1 M. hydrochloric acid.

5. **Cericsulphate, 3.3%** - Dissolve 16.5 g of ceric sulphate in 500 ml of 0.5 M sulphuric acid.
6. **Sodium bi sulphite 1%** - Dissolve 1 g of sodium bi sulphite in 100 ml of water.
7. **Rhodamine-B-0.02%** - Dissolve 0.02 g of rhodamine B in 100 ml of 1 m hydrochloric acid. Warm and filter, if necessary.
8. **Isopropylether** : Shake in a 500 ml separating funnel, sufficient isopropylether with successive 25 ml portions of ceric sulphate solution until the yellow colour remain after shaking for 1 minute. Then destroy the excess ceric sulphate with 1 ml 1% aqueous NH_2OH. HCl and discard the aqueous phase. Shake with two 25 ml. portion of water followed by 25 ml of 1 M HCl. Stopper the funnel and leave the ether standing over the hydrochloric acid, until required. This treatment should be repeated daily.
9. **Standard antimony stock solution Sb-1000 mg/ml** – Dissolve 0.11979 of antimony (iii) oxide, Sb_2O_3 in 100 ml of 6 M hydrochloric acid. Prepare antimony standard 100 mg Sb/ml by dilution of 10 ml of 1000 Mg/ml antimony solution to 100 ml with 6 M hydrochloric acid. Prepare an antimony solution containing 5 Mg.Sb/ml by dilution of 5 ml of 100 mg Sb/ml to 100 ml by 6 M hydrochloric acid (Prepare fresh).

Procedure

- Weigh 0.2 g sample into the test tube.
- Add 1 g potassium pyrosulphate and mix well.
- Heat in a flame until frothing ceases remove from the flame and spread melt in a thin layer on the wall of the tube.
- Allow to cool and add 5 ml of 6 M hydrochloric acid.
- Heat the tube gently in a steam bath untill the melt breaks up, taking care that the solution does not boil.
- Remove the tube and add 1 ml of 1% sodiumbisulphite solution.
- Make up to 10 ml with 6 M hydrochloric acid. Mix the contents and allow to settle overnight.
- Decant the solution into a 125 ml. Separating funnel. Wash the sides of the tube and residue in the 3 ml warm 6 M hydrochloric acid, allow to stand a few minutes and decant in the separatory funnel.
- Repeat above step with 3 ml of warm 6 M hydrochloric acid and then with 2 ml. of hot water.
- Cool the solution to below 25^{o}C.
- Add 5 ml of ceric sulphate solution, mix and leave for 30 seconds.
- Add 1 ml 1% aqueous $NH_2OH.HCl$ and leave for 1 minute.
- Add 45 ml of cold water.
- Now add 5 ml isopropylether, shake for 1 minute and allow to stand 5 minutes.
- Drain off all but 0.5 ml of the aqueous phase and add 2 ml of 1% $NH_2OH.HCl$ in 1 M hydrochloric acid shake for 30 seconds.
- Allow the phases to separate, discard the aqueous phase. Add 2 ml of 1 M hydrochloric acid and shake for 30 minutes.

- Discard the aqueous phase. Add 2 ml of the 0.02% rhodamin-B solution and shake for 30 seconds.
- Discard the aqueous phase and transfer the ether phase to an absorption cell.
- Measure the optical density of the solution at 550 nm against a Reference solution isopropylether. If the reading is greater than the highest calibration standard, pipette a suitable volume of the ether solution into an absorption cell and dilute as necessary with a known quantity of isopropylether record the dilution.
- From the optical density reading, determine the concentration of antimony from the calibration curve.

Preparation of standard curve

Add 15 ml of 6 M hydrochloric acid to each separating funnel containing 1,2,3 and 4 ml of 5 mg Sb/ml followed by 1 ml of 1% sodium bi-sulphite solution. Mix. Follow step (11) to (19). Record the optical density reading of each standard. Run-identical reagent blank. Construct the calibration curve by plotting absorbance against antimony concentration.

vii. Determination of small amounts of Vanadium ((V_2O_5) in Silicate rocks, Bauxite, Vanadium mineral, Iron ore, Red mud and Bayer plant liquored)

Principle

Estimation of vanadium (V) is based on the formation of yellow soluble phosphotungsto vanadic acid on treatment with phosphoric acid and sodium tungstate (tungstic acid) to an acid vanadate solution. The maximum absorption is at 400 nm.

Reagents

1. **Sodium tungstate 0.5 N :** Dissolve 16.5 gm of $Na_2WO_4.2H_2O$ in water and dilute to 100 ml.
2. **Standard vanadium solution :** 1 ml = 1 mg of V. Dissolve 1.785 gm of vanadium penta oxide (V_2O_5) in slightly excess of sodium hydroxide then add slight excess of dilute sulphuric acid and dilute to 1 liter**.**
3. **Sulphuric acid : (A.R. grade)**
4. **Phosphoric acid : (A.R. grade)**

Method of Decomposition : (Iron ore, Bauxite, Vanadium & Red mud) : Finally ground sample (0.10 to 0.20 gm) is fused with sodium carbonate in a platinum crucible and the sintered mass is leached with hot water. The filtered leach solution is fumed with perchloric acid for estimation of silica. The aliquot is used for determination of vanadium.

Alumina hydrate

The vanadium present as soluble salt is leached with hot water. The filtrate is acidified with sulphuric acid and used for determination of vanadium.

Calcined Alumina

The sample is fused with a mixture of borax and sodium carbonate and the sintered mass is leached with hot water and filtered. The filtrate is acidified with sulphuric acid and used as aliquot.

Bayer plant process liquors

The filtered sample is acidified with sulphuric acid and used as aliquot.

Procedure

- Transfer approximate aliquot (about 0.1 gm sample) in a 250 ml beaker.
- Add approximately 3 ml dilute 1:1 sulphuric acid and some water to bring volume about 40 ml and heat to 90-95°C (do not boil the solution). Add 2-3 drops acid in excess, adjust pH around 2-2.5.
- Add 5 ml 1:1 orthophosphoric acid.
- Keep for 5 minutes then add 0.5 ml of tungestic acid and again heat to 90-95°C.
- Allow the solution to stand for two minutes, cool to room temperature.
- Transfer the solution into 100 ml volumetric flask and make with water up to the mark.
- Measure the absorbance of solution at 400 nm.
- If titanium content is high as expected in bauxite read the absorbance after standing coloured solution for about an hour. During this course, colour of titanium complex fades completely.
- Calculate percentage of vanadium by using standard calibration curve.

Standard calibration curve

Place 0.5, 1.0, 2.0 and 2.5 ml of the vanadate standard solution, 1 mg vanadium/ml into fine 100 ml volumetric flasks. Then follow the procedure step 2 to 8. Construct the calibration curve using the data obtains.

viii. Determination of small amounts of Iron (In clay, quartz, silica sand/calcite samples, etc.)

Principle

Iron is determined by the complex formation of orange, red coloured complex with 1.10 phenathroline at pH about 3.5 in sodium citrate medium containing ascorbic acid as reducing a gent.

Reagent

1. **Standard solution:** Dissolve 1.00 gm of iron metal in 20 ml of 1:1 HCl and dilute 1 litre to get 1 ml = 1 mg iron solution.
2. **Ascorbic acid :** A.R. grade, 1% solution in water.
3. **Sodium citrate** : A.R. grade, 20% solution in water**.**
4. **1,10 – phenanthroline :** A.R. grade 0.25% solution in water.

Decomposition (Silicate rocks)

Finally powdered sample (0.1-0.2 gm) is fused with sodium carbonate and potassium carbonate (5:1) ratio mixture in a platinum crucible. Extract in water, dissolve in 1:1 hydrochloric acid if any insoluble matter. Bake, dry the solution, filter through No.40 filter paper, dis-card silica.

Alternately sample can directly be kept for hydrofluorisation. Weigh 0.1 gm sample in platinum crucible, add 5 ml water, 5 ml 1:1 H_2SO_4 and 1 ml hydrofluoric acid. Evaporate to dryness. Fuse with potassium pyrosulphate. Extract with 1:10 sulphuric acid, proceed with aliquot.

Iron : Add concentrate hydro chloric acid 20 ml to 0.4 gm sample. Add more from time to time as required till complete digestion. Make up the volume to 1 litre and appropriate aliquot**.**

Silica sand, quartz Take 0.1 gm sample in a platinum crucible, add 2-3 drops 1:1 sulphuric acid and 10 ml HF. Hydrofluorise till dryness. Repeat the process twice. fuse with potassium pyrosulphate and extract in 1:1 hydrochloric acid. Take aliquot for iron determination.

Procedure

- Take appropriate aliquot 10 ml. Neutralizxe the solution with 10% NaOH solution using phenolpthalien indicator exactly.
- Add 5-6 drops conc. hydrochloric acid with mixing to adjust the pH 3.0-3.5.
- Add 5 ml sodium citrate solution to set pH exactly 3.5-4.0.
- Add 2 ml of ascorbic acid to reduce Fe^3 to Fe^2.
- Add 5 ml of 1,10 phenanthroline solution.
- Keep the solutions for an hour. Make up the volume in 100ml. Volumetric flasks with water.
- Measure the absorbance at 500 nm. Run a reagent blank.

Standard calibration curve

Take 0.3, 1.0, 1.5, 2.0 and 4.0 ml of standard iron solution in 100 ml volumetric flask and follow the steps from 1 to 6. Plot the calibration curve and compute the results.

ix. Determination of small amount of manganese

Principle

The sample is decomposed with hydrochloric and nitric acid and fumed off with sulphuric acid. Phosphoric acid is added to complex with iron and it prevents precipitation of periodates or iodatas of manganese. Permanganate colour is developed by addition of potassium per iodata in boiling state. The absorbance is measured at 545 nm.

Reagent

1. **Standard Manganese Solution** Dissolve 1.00 gm of electrolytic manganese metal in dilute nitric acid by heating and make up in 1 litre. Alternately weigh 1.2255 gm. manganese dioxide in a 250 ml beaker, decolourize it by 15 ml HCl. add 20 ml 1:1 sulphuric acid, fume off completely. Extract in 10% sulphuric acid and make up to 1 litre in measuring flask to get 1 ml = 1 mg. MnO in solution**.**
2. **Potassium periodate** **:** Solid A.R. grade
3. **Hydrochloric acid** **:** A.R. grade
4. **Nitric Acid** **:** A.R. grade
5. **Sulphuric acid** **:** A.R. grade
6. **Orthophosphoric acid** **:** Manganese free (A.R. grade)

Procedure: Decomposition (silicate rocks, Mn ore, Bauxite) To, a 0.5 gm sample add 10 ml conc. hydrochloric acid and 2.0 ml conc. nitric acid, digest on hot plate. Extract in dilute HCl and filter through No.40 Whatman filter paper. Ignite the residue and hydrofluorise silica. Fuse the mass with potassium pyrosulphate and extract in hydrochloric acid and mix with main solution.

Alternately sample can directly be kept for hydrofluorisation in presence of 2 ml conc. sulphuric acid and 10 ml of hydrofluoric acid. Fuse with $K_2S_2O_7$. Extract in 1:10 H_2SO_4.

Alternately take suitable aliquot 10-25 ml.

1. From mother liquor, add 10 ml. conc. H_2SO_4, fume it off completely till syrapy mass, remains.
2. Extract in 10% sulphuric acid solution. (Filter off if any suspended matter).
3. Add 5 ml 1:1 orthophosphoric acid. The solution should be colourless at this stage.
4. Heat the solution to boiling, add at pinch (0.2-0) of potassium per iodata.
5. Develop permangate colour.
6. Cool the solution and make up 100 ml in measuring flask. Measure absorbance at 545 nm.
7. Run a reagent blank. Calculate percentage of MnO by using standard calibration curve.

Standard Calibration Curve

Take 0.10, 0.15, 0.20, 0.30 and 0.40 ml of standard MnO solution in 100 ml volumetric flasks. Follow the procedure from step 2 to 6. Plot the calibration curve and compute the results**.**

x. Determination of Small amounts of Phosphorous (P_2O_5 in Iron ore, Mn ore, Limestone, Silicate rocks)

Principle

A yellow mixed heteropoly acid molybdovanado phosphoric acid is formed when an excess of molybdate solution is added to an acidic (0.05 N HNO_3) solution of orthophosphate and vanadate ion. The absorbance is measured at 460 nm.

Reagents

1. **Standard phosphorus solution :** Dissolve 0.4263 gm diammonium hydrogen phosphate, $(NH_4)_2 HPO_4$ in water and make up the solution up to 1.0 liter to get 0.1 mg = 1 ml of phosphorus.
2. **Vanadate reagent :** Dissolve 2.5 gm ammonium vandate in 500 ml boiling water. Cool the solution and add 20 ml conc. nitric acid. Cool and dilute to 1 litre. Store in polythene bottle.
3. **Molybdate reagent :** Dissolve 50 gm ammonium molybdate tetrahydrate in warm water (50^oC). Cool and dilute to 1 litre. Store in polythene bottle**.**

Decomposition (Iron ore, Manganese ore & Limestone etc.)

Take 1.0 gm sample add 10 ml of conc. Hydrochloric acid heat on a hot plate to dissolve the sample. Add more acid if necessary. Cool and add 0.5 ml nitric acid, evaporate to dryness and bake carefully. Cool, add 3 ml conc. hydrochloric acid dilute with water boil and filter. Make the volume 100 ml use aliquot for further use.

Silicate Minerals : Take 0.10 gm sample in a teflon beaker. Moist the sample with 2-3 drops of water add 2 ml conc. HNO_3 and 10 ml hydrofluoric acid (40%). Heat at low temperature (~100^oC) and slowly evaporate to dryness. Add 1 ml nitric acid and evaporate to dryness (repeat this step once more time). Then take up the residue in 5 ml nitric acid and make up the volume 100 ml by water. Use appropriate aliquot for determination of phosphorus. Alternately sample can also be decomposed by fusion with potassium pyrosulphate at very controlled temperature (i.e. it should not go above 300^oC). Otherwise phosphorus may escape along with fumes. Take 0.1 gm sample, add 0.5 gm $K_2S_2O_7$ and fuse in temperature controlled conditions. Extract in 4M HNO_3 and proceed as follows.

Procedure

- Take 25 ml aliquot (~ 5 mg phosphorus per 25 ml) to a 100 ml. Volumetric flask.

- Add 5 ml of 1:2 nitric acid solution.
- Add 5 ml of ammonium vanadate solution.
- Add 5 ml of ammonium molybdate solution, dilute with water up to the mark and mix thoroughly and develop the colour.
- Keep the solutions for 10 minutes and measure the absorbance at 460 nm.
- Run a reagent blank.

Standard Calibration Curve

Take 1.0, 2.0, 3.0, 5.0 and 10.0 ml standard phosphorus solution (1 ml = 0.10 mg) in 100 ml volumetric flasks and run a blank also. Follow the steps 2 to 5. Plot the calibration curve and compute the results.

xi. Determination of Small amount of Titanium
(TiO_2 in silicate rocks, bauxite, clay, etc.)

Principle

A yellow coloured complex is formed by Ti(iv) with hydrogen peroxide in sulphuric acid and phosphoric acid medium. The absorbance is measured at 400 nm.

Reagents

1. **Standard TiO_2 solution**. Roast 1.0 gm of titanium dioxide (TiO_2) at 900^oC for 30 minutes. Transfer TiO_2 to 400 ml beaker. Add 20 ml conc. H_2SO_4 and 5.0 gm ammonium sulphate. Heat on hot plate at moderate temperature till a clear solution forms. Cool to room temperature and add 100 ml of water carefully and dilute to 1 litre. 1 ml = 1 mg TiO_2. Alternately, fume 3.5005 gm of K_2TiF_6 with 20 ml H_2SO_4 cool to room temperature and add 100 ml of water carefully. Finally make volume to 1 litre 1 ml = 1 mg TiO_2.

2. **Sulphuric acid :** A.R. grade
3. **Orthophosphoric acid :** A.R. grade
4. **Hydrogen per oxide solution** : 20 volume

Decomposition

1.0 gm sample is fused with 0.5 gm of potassium pyrosulphate in a test tube. Extract the mass with 1:10 sulphuric acid solution.

Alternately take direct appropriate aliquot from mother liquor after silica estimation add 10 ml 1:1 sulphuric acid, fume off completely till syrapy mass remains cool and extract in 1:10 sulphuric acid solution.

Procedure

- Take suitable aliquot in 100 ml volumetric flask in sulphuric acid medium.

- Add 10 ml of 1:1 orthophosphoric acid which forms colourless complex with iron.
- Add 2 ml of hydrogen peroxide (30% solution)
- Develop the colour. Make up the volume to 100 ml with water.
- Measure the absorbance at 400 nm. Run a reagent blank.

Standard Calibration Curve

Take 0.5, 1.0, 1.5, 2.0, 4.0, 6.0 and 10.0 ml standard TiO_2 solution in 100 ml volumetric flasks. Follow the steps from 2 to 5. Plot the calibration curve and compute the results.

xii. Spectro-photometric method for the Determination of traces of Germanium in ore and beneficiation products of Lead and Zinc.

Scope

This method is applicable to sulphide ores and beneficiation products of zinc and lead. The lowest level of GeO_2 determinable is 100 ppm**.**

Reagents and Standards

1. **Quality of reagents :** Unless otherwise specified analytical grade reagents and distilled water should be used.
2. **Standard germanium solution -** Dissolve 0.1000 gm pure GeO_2 (99.99%) in 20 ml of 10% sodium hydroxide dilute to 100 ml with water. Prepare the 10 mg GeO_2/ml from the above stock solution by adopting suitable dilution in 50% hydro chloric acid.
3. **Hydroxylamine hydrochloride (10%) solution** – Dissolve 10 g. hydroxylamine hydrochloride in 100 ml. water.
4. **Gum arabica** – (0.5%): To boiling water add 0.500 g gum-arabica, stir till it is completely dissolved cool and filter it, if necessary. This solution should be prepared fresh.
5. **Phenyl fluorine reagent (0.06%)** – To 60 mg. of phenyl fluorine in a beaker (250 ml) add 80 ml Ethyl alcohol followed by 5 ml. 1 : 6 sulphuric acid. Dissolve and transfer quantitatively to 100 ml. Volumetric flask. Make up the volume with alcohol.

Spectrophotometer: UV = visible spectrophotometer with tungsten lamp source is used.

Procedure

(A) Decomposition of Sample.

- Heat a sample weighing 0.5-1.0 g in a porcelain dish in a muffle furnace at 400-500°C. Trnasfer the residue to a platinum dish. Treat the sample with 5 ml sulphuric acid, 1 ml conc. nitric acid and 10 ml of hydrofluoric acid.

Heat it and evaporate to fumes, avoid prolonged or strong fuming with sulphuric acid. Cool and add 20 ml water and heat to near boiling for a few minutes. Cool and filter through Watman filter paper No.42, wash residue (lead sulphate and barium sulphate, etc.). with 1% sulphuric acid solution. Use filtrate for spectro-photometric determination.

- Alternatively, transfer 1.000 g sample (ground to 150 mesh) into a nickel crucible containing 4-5 g sodium peroxide. Keep the crucible on a wire gauge and heat by a burner till peroxide melts. Fuse the sample with flux for 5-7 minutes. Cool the melt in crucible. Transfer crucible to a 250 ml beaker containing 50 ml hot water. Boil, remove the crucible from beaker and wash with water. Evaporate the solution to 20 ml volume and transfer to the distillation flask. Assemble distillation unit and keep the receiving cylinder in ice-bath. Add 60 ml conc. hydrochloric acid. Boil and collect 45 ml of the distillate in a 6 N hydrochloric acid in cylinder. Make the volume 100 ml.

(A) Development of colour

For (i) – Take sufficient aliquot containing 10-50 mg. Germanium in a 150 ml separating funnel. Add conc. hydrochloric acid to attain an acid concentration of 9 M, mix and cool. Add 10 ml of carbontetrachloride, shake vigorously for two minutes. Transfer the organic layer to a 50 ml beaker, and repeat the extraction twice with 10 ml portion of carbontetrachloride. Combine the organic extracts in a 150 ml separatory funnel. Add 5 ml water containing 1-2 drops of 0.01 M sodium hydroxide shake for 2 minutes. Transfer aqueous phase to a 50 ml volumetric flask. Repeat extraction of organic phase twice with 5 ml water containing 1-2 drops of sodium hydroxide (0.01 M) and transfer to volumetric flask. Add 10 ml 6 M hydrochloric acid to the solution and mix.

For (ii) – Take 10 ml aliquot into a 50 ml volumetric flask.

Add 10 ml hydroxylamine solution and 5 ml gum arabica solution to the solution in 50 ml volumetric flask. Dilute to 40 ml with water and cool in an ice bath for 15 minutes. Add 2.5 ml phenyl fluorine solution and mix. Allow the solutin to attain room temperature (1 hour) and make up to the mark with water and mix. Measure the absorbance of the complex at 510 nm against reagent blank. Compute the GeO_2 content present in the sample from the calibration curve.

Calibration curve :

Take 1.0, 2.0, 3.0, 4.0 and 5 ml. of standard GeO_2 (10 Mg/ml) in 50 ml volumetric flask. Add 10.0, 9.0, 8.0, 7.0, 6.0 and 5.0 ml of 6 N hydrochloric acid, respectively. Add 10 ml hydroxylamine solution, 5 ml. Gum arabica solution and dilute to 40 ml. Cool in ice-bath. Remove the flask from ice bath. Add 2.5 ml of phenyl fluorine solution, mix and allow to cool to room temperature (1 hour). Make up the volume with water and measure the absorbance of the standards against the reagent blank at 510 nm. Draw the calibration curve by plotting the absorbance against the GeO_2 content. An absorbance of 0.149 unit observed for 10 Mg GeO_2/50 ml solution.

Calculation

$$\% \; GeO_2 = \frac{GeO_2 \text{ Mg x Dilution factor x } 100}{10^6 \text{ x Weight of sample (g)}}$$

or

$$GeO_2 \text{ (ppm)} = \frac{GeO_2 \text{ Mg Reading x Dilution factor}}{\text{Sample Weight (g)}}$$

$$\text{Dilution factor} = \frac{\text{Volume of solution made up}}{\text{Volume of aliquot taken}}$$

xiii. Spectrophotometric Determination of Gallium in Zinc and Lead ores and beneficiation products.

Scope

The method is applicable for determination of gallium in ore and mineral dressing products of lead and zinc.

Principle

Rhodamine-B reacts with chlorogallate anion to produce red-colour complex extractable in 3:1 chloroform carbon tetrachloride. The optical density of red chlorogallate-rhodamine-B complex in organic phase is measured at 565 nm.

Reagents and Standards

1. **Titanous chloride solution (20%)** – Treat pure titanium metal piece with hot conc. hydrochloric acid. Keep solution over titanium metal.
2. **Chloroform: Carbon tetrachloride (3:1) :** Mix 150 ml chloroform with 50 ml carbon tetrachloride.
3. **Rhodamine-B** : Dissolve 0.500 g rhodamine-B in 100 ml 6N hydrochloric acid.
4. **Di-isopropyl ether :** Pre extracted with 6N hydrochloric acid.
5. **Standard gallium stock solution** – Dissolve pure gallium chloride in 10 ml 6N hydrochloric acid. Transfer to a 100 ml volumetric flask, add 5 ml conc. hydrochloric acid and dilute to mark with water. This solution contains 1.0 mg Ga/ml in 6N hydrochloric acid.
6. **Standard Gallium working solution** – Prepare a dilute solution containing 1 Mg Ga/ml by serial dilution of the stock solution with 6N hydrochloric acid.
7. **Sodium chloride solution (1%)** : Dissolve 10 g sodium chloride in 100 ml water.

Procedure

(i) Decomposition of Sample :

Weigh 1-2 g of sample (-150 mesh) into a porcelain dish and roast at 500°C for 3 hours in a muffle furnace. Cool the dish transfer the sample into a 250 ml beaker. Add 50 ml aquaregia, cover the beaker and keep aside for half an hour. Digest on steam bath for half an hour. Remove the watch glass. Wash with water and evaporate the solution to dryness with occasional mixing. Add 50 ml of 6 M hydrochloric acid, boil to dissolve the residue. Filter through Whatman filter paper No.40 containing a little pulp into a 100 ml volumetric flask. Wash the residue with 6 M hydrochloric acid make up the volume 100 ml maintaining 7 N hydrochloric acid concentration.

(ii) Separation of Gallium

Take 10 ml aliquot in a 100 ml separatory funner, add 2 ml titanous chloride solution, mix after 5 minutes, add 10 ml di-isopropylether and shake for 1 minute. Run the lower aqueous phase into another separatory funnel and shake aqueous phase with 5 ml of di-isopropylether. Repeat extraction twice with 5 ml portion of di isopropyl ether. Discard aqueous phase. Wash combined organic extract with a mixture of in hydrochloric acid and 0.5 ml titanous chloride solution twice. Transfer organic layer to a 100 ml beaker. Add 0.3 ml of sodium chloride solution and evaporate ether on steam bath. Take up residue in 5 ml M HCl and transfer to a 100 ml separating funnel. Dilute it to 25 ml keeping acid concentration to 6N hydrochloric acid. Add 0.4 ml rhodamine solution and 10 ml of 3:1 chloroform carbonate trachloride. Shake for 1 minute. The lower organic layer is transferred to an absorption cell of spectrophotometer. Read absorbance of red complex at 56 nm against a reagent blank in organic phase. Calculate gallium content from calibration curve.

Calibration Graph

Take 0.0, 1.0, 2.0, 3.0, 4.0 and 5 ml of standard gallium solution (1 Mg/ml) in separatory funnels. Add 25, 24, 23, 22, 21 and 20 ml of 6 M HCl, respectively. Add 0.4 ml rhodamine-B solution and 10 ml of chloroform carbon tetrachloride mixture. Shake for 1 minute. Let separate organic layer, filter and read absorbance at 565 nm. Construct a calibration graph by plotting absorbance against Mg gallium concentration. An absorbance of 0.08 units is found for 1 mg gallium/10 ml volume.

Calculation

$$\text{Gallium Mg/ml} = \frac{\text{Mg gallium reading x Dilution}}{\text{Sample weight (g)}}$$

Preparation of Reagents

1. **Acid mixture -** To 60 ml water, add 15 ml conc. H_2SO_4 and 15 ml H_3PO_4, cool and dilute to 1 litre.

2. **Acetic Acid** – **Ammonium Acetate Buffer solution pH 5.5** -Take 200 g. Of ammonium acetate and 30 ml. acetic acid, make the volume to one litre. Check the pH with pH meter or pH paper and adjust the pH 5.5 either by acetic acid or ammonia.

3. **Ammonium Molybdenum solution 12% (W/V**)-Dissolve 12 g. Ammonium molybdate tetrahydrate $(NH_4)_6$ $MO_7O_{24}.4H_2O$ in a water and dilute to one litre. Allow the solution to stand for one day and filter**.**

4. **Bromine tetrachloride solution** -Carbon tetrachlorite saturated with bromine.

5. **Bromine – potassium bromide solution** -320 g of potassium bromide is dissolved in just sufficient water and 200 ml bromine added. After mixing well, the solution is diluted to 2 litre.

6. **Buffer solution pH 9.5** -Dissolve 67.5 g of AR NH_4 Cl in 300 ml water, add 570 ml NH_4OH and dilute to one liter with distilled water.

7. **Buffer solution** – **(Monochloroacetic acid pH 2.9 – 3.1)** Dissolve 18.9 g of monochlora acetic acid in distilled water and dilute to 200 ml., neutralize 100 ml. to phenolpthelein end point with NaOH and add to remaining 100 ml. Dilute to 500 ml. with distilled water, check the pH with pH meter.

8. **2'-2' biquindine –** 100 g in 500 ml. amyl alcohol

9. **Citromolybdate reagent -** Stir 54 g of AR MoO_3 with 200 ml. distilled water, add 11 g of NaOH gradually and stir it while heating until Molybdic anhydride is dissolved. Dissolve 120 g of pure citric acid in 250-300 ml water and 140 ml. pure HCl of Sp.Gr. 1.19 and add molybdate solution to the acid solution while stirring, cool and filter through a pulp pad, if necessary, and dilute to one litre. The solution is blue or green in colour. Add drop wise a dilute 0.5-1%. solution of $KBrO_3$ until the blue colour disappear.

10. **Diphenyamine barium sulfonate** -Dissolve 0.25 g in 100 ml. water

11. **Dimethyglyoxime (sodium salt) –** 10% (W/V) in water

12. **1-5 diphenyl carbazide 0.25%** -Dissolve 0.25 g of $(C_6H_5NH.NH)_2CO$ in 100 ml. 95% ethyl alcohol or 50% acetone or isopropyl alcohol.

13. **H_2SO_4 2.5 M –** Add 130 ml. of conc. H_2SO_4 slowly while stirring to 800 ml. of water. Allow the solution to cool and make up to one litre in a measuring flask.

14. **H_2SO_4 6 N** – Add cautiously 167 ml. of conc. H_2SO_4 to distilled water and dilute to one litre**.**

15. **Hydroquinone –** 1% (W/V) in water**.**

16. **λ-nitroso- B naphthol solution** is prepared in 1:1 acetic Acid.

17. **Mercuric chloride –** Saturated solution in water (60-80 gm./litre)

18. **5% Mercuric chloride –** 50 g of $HgCl_2$ in 1 litre**.**

19. **Molybdate reagent –** Dissolve 50g of ammonium molybdate in water and dilute to one litre.

20. **Orthophenonthroline** – 0.25% in distilled water.

21. **Oxalic acid 5% W/V –** Dissolve 50 g of oxalic acid in 500 ml. water and dilute to one litre. Filter the solution if necessary. Always prepare fresh solution.

22. **Nitroso – R salt – (Sodium nitroso 2.hydroxy naphthalene 3, 6 disulphonate –** 0.2% aquous solution.

23. **Potassium Thiocyanate (20%) –** Dissolve 20 g of potassium thiocyanate in100 ml. water. This reagent should be prepared fresh daily.

24. **Potassium hydroxide(20%) –** Dissolve 20 g of AR quality of AR KOH in 100ml. water.

25. **Quinoline hydrochloride solution –** Take 60 ml. conc. HCl and 300-400 ml. water in one litre beaker and warm it to 70-80^{o}C. Pour 50ml. synthetic pure quinoline (free from reducing agent) in a thin stream into the dilute acid. When quinoline has dissolved cool the solution and dilute to one litre, filter through paper pulp.

26. **Stannous chloride solution –** Dissolve 5 g of stannous chloride pure AR quality in 25ml. conc. HCl and dilute to 100 ml.

27. **Sodium citrate –** 250 g in one litre of distilled water.

28. **$SnCl_2$ 2M –** Dissolve 113 gm of $SnCl_2$(AR) dihydrate in conc. HCl and make up to 250 ml. with conc. HCl.

29. **Starch Solution –** Mix about 1 g of soluble starch with about 20 ml. of cold water and add the mixture slowly to 80 ml. boiling water. Boil for a few seconds. Prepare fresh solution when required**.**

30. **Tartaric Acid –** Dissolve 75 g of tartaric acid in one litre of water.

31. **Vanadate solution** – Dissolve 25 g of ammonium vanadate in boiling water and cool the solution. Add 20 ml. conc. HNO3, cool and dilute to one litre.

32. **Xylenol orange – (0.2%)** – Dissolve 0.2 g of reagent in water, add 1 drop of 1:1 HCl and make up the volume to 100 ml.

Common acids and alkalies – Useful data

	HCl	HBr	HNO_3	HF	$HClO_4$	H_2SO_4	H_3PO_4	CH_3COOH	NH_4OH
Molecular weight	36.46	80.92	63.02	20.01	100.46	98.07	98.00	60.03	35.04
Average Sp.Gr. of conc.reagent	1.19	1.49	1.42	1.15	1.68	1.84	1.69	1.06	0.90
Average % present in conc.reagent	36.0	48.0	69.5	48.0	71.0	96.0	85.0	99.5	58.6
Concentration of concentrated reagent (MOLARITY)	11.7	8.8	15.6	27.6	11.8	18.0	14.7	17.6	15.1
Ml. of concentrated reagent per litre of 1 M soln.	85.5	113.6	64.0	36.2	84.4	55.6	68.2	56.9	66.5
Grams of active ingradient per ml.	0.426	0.715	0.985	0.552	1.19	1.77	1.44	1.0555	0.527

Standard Solution and Standardization

1. **Alumnium solution –** Dissolve 0.2646 g of very thin aluminium foil or wire in 10 ml. conc. HCl and make up to 500 ml.

   1 ml = 1 mg. Al_2O_3

2. **Arsenite solution 0.1N –** Dissolve 4.9455 g of As_2O_3 in a warm solution 2-3 gm. of pure NaOH in 30-40 ml. water. The solution is made slightly acidic with HCl or H_2SO_4.

3. **Bismuth solution** – Dissolve 0.25 g of bismuth (pure) metal by heating with 30 ml. of 30 of HNO_3. Boil the solution gently for 10 min, then cool and dilute to 250 ml. with water.

4. **Calcium standard solution** – Weigh 1.7857 g of AR $CaCO_3$ dried at 150°C in a beaker, add 50 ml. water and dissolve in 10.6 ml. HCl added in small increment. When dissolution is complete, boil the solution to remove CO_2. Cool the solution to room temperature, transfer to a litre volumetric flash and dilute to the volume with water.

   1 ml = 1 mg. CaO

5. **Chromium solution** – Dissolve 2.8283 g of pure $K_2Cr_2O_7$ in water and dilute to a litre in a volumetric flash. Pipette 20 ml. of this solution into a 2 litre volumetric flash and dilute to the mark with water.

   1 ml = 0.01 mg. Cr.

6. **EDTA solution (0.05 M)** – Dissolve 327.24 g of di-sodium salt of EDTA in a water finally make up the volume to 20 l. It is advisable to allow EDTA solution standing for couple of days.

7. **Ferrous Ammonium sulphate** (0.1 N) $(NH4)_2SO_4$ $FeSO_4$ $6H_2O$ –

   Dissolve 39.213 g of ferrous ammonium sulphate in a water and add enough H2SO4 to prevent hydrolysis (aliquot 10 ml. per litre). Standardize by titration with standard dichromate solution.

8. **Ferric Ammonium sulphate solution** – Fe_2 $(NH_4)_2SO_4.24H_2O$

   Dissolve 60 gm. of the salt in 600 ml. water acidified with 20 ml. of 1.1 H_2SO_4. Add $KMnO_4$ solution until a pink colour begins to appear. Dilute the solution to 2 litres. Standardize against 0.1N $K_2Cr_2O_7$ solution to find out the exact strength.

9. **Fluoride solution** – Dissolve 2.211 g of sodium fluoride (AR) previously dried at 120°C to constant weight in one litre of water in volumetric flash.

   1 ml = 1 mg. of F

10. **Hydrochloric Acid 0.1 N –** Take 9 ml. conc. HCl sp.gr. 1.19 and dilute to one litre with DM water. This will give approximately 0.1 N hydrochloric acid solution.

11. **Iodine solution 0.1 N**- Dissolve 20-25 g of KI in minimum water and add 12.7 g of Iodine (resublimed, theoretical value 12.692 gm) and dilute to 1000 ml. after all of the iodine has been dissolved in the small volume of KI solution. Preserve in dark bottle.

12. **Magnesium standard solution** – Dissolve 0.6033 g of Magnesium ribbon in conc. HCl in a beaker and make up to one litre with distilled water.

    1 ml = 1 mg. MgO

13. **Manganese standard solution** – Dissolve electrolytic manganese metal in 40 ml conc. HNO_3 by heating cool dilute to one litre in volumetric flask. Transfer 50 ml. of this solution to a one litre volumetric flask, add 50 ml HNO_3 and dilute to the volume.

    1 ml = 0.05 mg of manganese

14. **Molybdenum standard solution –**

    Dissolve 0.075 g of AR MoO_3 in dilute sodium hydroxide, dilute with water and make slightly acidic with HCl and make up to 500 ml. with water.

    1 ml = 0.0001 g of Mo
    = 0.1 mg. of Mo

15. **P_2O_5 standard solution –** Dry potassium hydrogen phosphate KH_2PO_4 at 110°C. Weight 0.9588 g and dissolve in water. Add 5 ml. HNO_3 and dilute to 500 ml.

16. **Potassium dichromate solution 0.1 N –**

    Dry AR quality potassium dichromate at 105-110°C cool in a desiccators and weigh 4.904 g dissolve in water, add 0.5 ml dil.H_2SO_4 and make it one litre in a volumetric flask.
    It is necessary to standardize $K_2Cr_2O_7$ solution against standard iron ore solution**.**

17. **Potassium permangnate solution –** Take 3.2 to 3.25 g of potassium per mangnate and dissolve in one litre of hot water. After standing 12 hrs. or longer the solution is filtered through glass wool in order to free it from manganese dioxide which catalyzes the decomposition of the reagent.

18 **Silica standard solution –** Fuse 0.1gm.of pure silica with 0.5 g of anhydrous sodium carbonate in a platinum crucible, cool the melt. Dissolve in water and dilute to one litre and store in polythene bottle.

1 ml = 0.1 mg. of SiO_2

19 **Sodium thiosulphate standard solution** –

Dissolve 25 g of sodium thiosulphate in hot distilled water that has been just boiled to expel CO_2. Add 0.1 g of sodium carbonate. Cool and make up to 1 litre. Addition of sodium carbonate increases the life of solution. Actually as per the reaction i.e.

$I_2 + 2Na_2S_2O_3 = 2 NaI + Na_2S_4O_6$

24.815 g of $Na_2S_2O_3$ is required to prepare 0.1 N solution**.**

20 **Silver nitrate standard solution –**

This solution contains 10.788 gm. of silver or 16.989 g of silver nitrate per litre. The silver nitrate dried at 120°C. The required weight of the latter may be dissolved in HNO_3 and make up to one litre. It is standardized against pure NaCl solution (0.1 N).

21 **Sodium Tungstate solution (0.5 N) –**

Dissolve 16.5 gm of $Na_2WO_4.2H_2O$ in water and dilute to 100 ml.

22 **Thorium nitrate standard solution –**

Weigh 13.806 g of thorium nitrate $Th(NO_3)_4.4H_2O$ dissolve in water and make up to one litre. Mix well standardize against fluoride solution.

23 **Vanadium standard solution** –

Dissolve 1.785 g of pure V_2O_5 previously ignited at 500°C in a slight excess of sodium hydroxide, add slight excess of H_2SO_4 and dilute to one litre. This solution contains 1 mg. of vanadium per ml.

24 **Zinc Acetate solution** (Approximately 0.05 M) –

Dissolve 50 g of AR quality zinc acetate in 500 ml. of hot water and make up the volume to one litre with distilled water. Add two or three drops of dilute acetic acid to make the solution clear.

Standardization of HCl solution

Weigh 0.2g of dried sodium carbonate (at 105°C for 30 minutes) in 250ml. beaker. Add 100 ml. DM water. Shake with glass rod to dissolve the solids. Add 2-3 drips of methyl orange indicator solution. Titrate this against the hydrochloric acid solution. The colour changes from yellow to orange.

$$\text{Normality of HCl} = \frac{\text{weight of } Na_2CO_3 \text{ x } 1000}{\text{Equivalent wt. of } Na_2CO_3 \text{ x titer value(ml)}}$$

Al_2O_3 equivalent of zinc acetate solution

Take 5ml standard aluminium solution (equivalent of 5 mg. of Al_2O_3) in a beaker. Add 25 ml. EDTA solution and make up the volume to nearly 200 ml.Adjust the pH to 5-5.5 by adding buffer and boil for 10 minutes. After cooling add 50 ml, 5.5 pH sodium acetate buffer boil for 10 minutes and after cooling add a few drops of xylenol orange indicator when yellow colour will develop. Titrate with zinc acetate solution to the purple end point.

$$\text{1 ml zinc acetate solution} = \frac{5 \text{ g } Al_2O_3}{\text{(A-B) X } 1000}$$

Where

A = ml zinc acetate equivalent to 25 ml. of EDTA soln.
B = ml zinc acetate solution required for titration after adding 25 ml. EDTA solution to the 5 ml standard Al_2O_3 solution.

Standardization of EDTA (0.05 M) for Pb:

The lead value of 1ml. EDTA solution is determined either from a synthetic or Cu-Pb-Zn standard sample.

Standardization of EDTA for CaO & MgO

Take 20-25 ml standard Ca solution in a beaker. Add a pinch of hydroxylamine hydrochloride and 10ml. triethanal amine solution and 10-20 ml KOH solution and a few drops of Patton and Reeder's indicator. Also add 1 ml. standard magnesium solution. A rose red colour will develop. Titrate the resulting solution with standard EDTA solution till a blue colour is detained. Note the reading. The EDTA used up is due to CaO only.

$$\text{Molarity of EDTA solution (M EDTA)} = \frac{\text{Mass of calcium in aliquot taken (g)}}{0.04008 \times V}$$

Where V = volume (ml) of EDTA solution required by the calcium.

Calcium equivalent (mg/ml) of EDTA solution

$$(\mathrm{Ca})_{\mathrm{Eq}} = \text{M EDTA} \times 40.08$$

or

$$\frac{\text{Mass of calcium in aliquot taken (mg)}}{V}$$

Where V is as stated above

% Ca in a sample

$$= \frac{Vs \times Ca_{(Eq)} \times 100}{S}$$

where V_s = volume (ml) of EDTA solution required for the titration of Ca.

S = Mass of the sample with aliquot.

$V_{Mg} = Vt-Vs$

Where VT = Volume (ml) of EDTA solution required for the titration of calcium plus magnesium.

Vs & S are as described above.

Similarly for magnesium take standard magnesium solution (20-25 ml) in a beaker. Add nearly 50 ml. distilled water and 25 ml. buffer solution. Add a spetula of hydroxylazmine hydrochloride and 5-10 ml. triethanolamine and then a few drops of Eriochrome black T indicator. A port wise colour will develop. Titrate with EDTA till a blye black colour end point is obtained. Take the reading.

The EDTA used up is due to CaO + MgO

Magnesium equivalent (mg/ml) of EDTA solution

$(Mg)_{Eq}$ = M EDTA x 24.31

Or

$$= \frac{\text{Mass of Magnesium in aliquot taken (mg)}}{V_{mg}}$$

Where V_{mg} = Volume of EDTA solution required by magnesium.

It is preferable to find out 1 ml. EDTA equivalent of CaO & MgO by taking standard sample of dolomite or limestone.

$KMnO_4$ – Standardization against Sodium Oxalate

Eq.Wt. = 67 dried at 105°C

Transfer 0.1 gm. of pure sodium oxalate – dried at 105-110°C for 1-2 hr. to a 250 ml. beaker or conical flask containing 15-20 ml. 10 of H_2SO_4 and about 100 ml. water which was previously boiled for 10 minutes and cool to room temperature. Shake with glass rod or swirl if it is in a flask until the oxalate is dissolved, then heat the resulting solution 70-80°C and titrate with standard potassium permanganate solution until a faint pink colour persists for about 30 seconds.

$$N = \frac{\text{Wt of sodium oxalate x 1000}}{\text{Eq. Wt. of sodium oxalate x T.V.}}$$

T.V. = Titre value.

Standardization of Iodine solution:

Aliquot portion are titrated with standard thiosulphate or with standard arsenite. Alternatively separate weighed portion of primary standard arsenious oxide may be dissolved and titrated.

As_2O_3 Eq.wt. = 49.455 gm.

Sodium thiosulphate solution: (0.1 N)

Sodium thiosulphate reacts with iodine as follows:

$I_2 + Na_2S_2O_3 = 2\ NaI + Na_2S_4O_6$

So 24.815 gm. of $Na_2S_2O_3.5H_2O$ is required to prepare 0.1 N solution

Standardization of Sodium thiosulphate solution:

It is standardized against standard dichromate solution.

Take 4.9035 gm of $K_2Cr_2O_7$ per litre. Take an appropriate volume of this 0.1 N solution into water containing 2-3 gm. of KI and 10 ml. dil. HCl per 200 ml. The acid solution should be freed of dissolved air. The iodine liberated is titrated with thiosulphate solution and the normality is determined.

1.7 General safety precautions

Precautions for safety are essential in an analytical laboratory, where corrosive acids, caustic alkalies, hazardous chemicals, brittle glassware, etc. are handled as a daily routine. It is the responsibility of every worker to be cautious and vigilant to avoid acts that may lead to injury to himself or to his colleagues. An attempt is made to provide a few basic guidelines for safety.

A. Personal wear

Loose clothing should not be worn, as it may knock down glassware, spurting acids and chemicals or catch fire from the numerous burners in the laboratory. Laboratory coats or aprons should be used as they protect the dress from acid holes or contamination with chemicals. Ladies should wear long overcoats to protect their saris. The hair should be well tied up and should not hang loosely. Plastic or rubber apron may be used, when handling large quantities of acids or corrosive chemicals.

It is advisable to use rubber gloves when handling corrosive liquids like bromine, fuming nitric acid, hydro-fluoric acid, etc. Asbestos gloves should e used, while removing crucibles from furnaces. If, by accident, some acids or chemicals spill over the dress, the clothing should be removed and a shower taken to guard against the possibility of reaction with skin. Safety glasses are also recommended for eye protection. Shoes are to be worn as footwear.

B. Handling of glassware

Glassware presents an hazard due to the ease with which it is broken by thermal or physical shock and the razor-sharp edge which the broken glass presents. Small beakers should be carried by gripping around the sides and not by the top edge. While using pipette, the worker should be very attentive not to draw the solution inside the mouth. In case of poisonous chemicals, the pipette should be filled by vacuum suction and not by mouth. While heating the test tube, the proper holder should be used and test tube mouth should not point at anyone, as the material may spurt out. Rubber tubing on glass tubes should not be pulled out with hand. Instead it should be cut out with a sharp knife. Stiff stopcock of burettes should be removed by light tapping or by warming it over gentle heat and not by application of force. Patience is essential if breakage and injury are to be avoided. All the broken glassware should be discarded into a separate metal container for disposal.

C. Handling of chemicals

Virtually, all chemicals react with human system. Hence, the analyst should handle the chemicals with great care.

Strong oxidizing agents such as perchlorates, sodium peroxide can cause fire or explosion when reacted with some organic materials. These reagents must be handled carefully. Do not use per chlorate for drying organic materials.

While fusing with sodium peroxide in a nickel crucible, a tray containing thick layer of sand should be kept nearby. If during fusion, the crucible develops a hole, it should be plunged into the sand. It should not be thrown away or plunged into water, as serious explosion may occur. Fuming with acids should Invariably be done in the fume cupboard and not on the work benches.

Acids should not be stored along with alkalis like ammonia. Concentrated sulphuric acid bottles should be kept separate and handled with care. Perchloric acid which is commonly used nowadays, should be kept in a lead lined box filled with sand and away from any organic materials. If fuming nitric acid is splashed over inflammable materials such as straw, wood, etc., they will immediately catch fire. Such acids should be kept in a box containing sand. Finely divided zinc or sulphur, if thrown in wastebasket, may cause delayed fire due to spontaneous combustion.

Potassium cyanide is widely used for limestone analysis. It should always be kept under lock and key. Cyanide solution should always be used in the alkaline medium. Cyanide solution should never be used in acidic medium. The waste solution should be collected in a bucket and cyanide ions should be destroyed by adding either bleaching powder or chlorine in alkaline medium, before disposal. On disposal, it should be flushed with plenty of water. Under no circumstance, cyanide solution should be drawn by mouth into a pipette.

Every container of chemicals must be clearly labeled. Abbreviation should be avoided as far as practicable. The label should be on the container itself, not on the lid.

D. Handling of compressed gas cylinders

Acetylene and Nitrous oxide gases are used with atomic absorption spectrophotometer. While installing a new cylinder, the leakage of the gas should always be tested with a solution of soap. Cylinder having leakage should immediately be returned. The room should be provided with adequate exhaust arrangements.

While using nitrous oxide, ice condenses in the tube after a while. This may block the gas and lead to explosion. A heating tape should be wound round the outlet of the gas. Great precautions should be taken while working with this gas, as its inhalation is dangerous. Stiff valves should be opened with care. If the cylinder valve cannot be operated by hand, it is unwise to resort to the use of hammers. On no account should oil or grease be used in an attempt to ease the working of the valve.

E. Eating and drinking in the laboratory

Food and beverage should never be consumed or stored in an analytical laboratory. Warming the lunch in an oven or over burners or taking cold water from the refrigerator wherein chemicals are stored should never be practiced. Beaker, conical flask, etc. should never be used for tea, coffee, or other beverages. Such beakers and conical flasks might be contaminated with poisonous chemicals. Smoking in a laboratory is also inadvisable and particularly in airconditioned rooms, where sophisticated instruments are in use.

F. Working along in the laboratory

Working alone in a laboratory is not desirable as an injury or illness could occur and help might not be available readily. Even the simplest of experiments have been known to cause serious accidents.

Titre equivalents per ml. of standard solution

1 ml N $KMnO_4$	0.05585 gm. Fe
1 ml N $K_2Cr_2O_7$	0.07185 gm. FeO 0.07985 gm. Fe_2O_3
1 N $KMnO_4$	0.01648 gm Mn (Volhard's 3/10 Mn) 0.01029 gm. Mn (Bismuthete per sulphate calorimetric per iodate) 0.04347 gm. MnO_2 ($FeSO_4$, Oxalic acid Method $MnO_2/2$) 0.02804 gm. CaO 0.032 gm. Mo by Jone's reductor Mo^{vi} - Mo^{iii} 0.02534 gm. Cr_2O_3 ($Cr_2O_3/6$) 0.06057 gm Sb 0.0435 gm MnO_2 0.07490 TiO_2
1 ml. N $Na_2S_2O_3$	0.06357 gm. Cu 0.06907 gm. Pb (Pb/5) 0.01603 gm S By evolution method 0.04395 gm FeS
1 ml. of N Iodine	0.05955 gm. Sn 0.03746 gm. As
1 ml. of N HNO_3	0.001349 gm. P Nitromolybdate 0.003086 gm. P_2O_5 method
1 ml. of N HCl	0.001193 gm. P Citromolybdate 0.002733 gm. P_2O_5 method
1 ml. of N Ferric Amm. Sulphate	0.08 gm. TiO_2

Appendix III

Conversion factors

FROM	TO	MULTIPLY BY
Al_2O_3	Al	0.5293
$AlPO_4$	Al	0.2212
$AlPO_4$	Al_2O_3	0.4180
$BaCO_3$	Ba	0.6960
$BaSO_4$	S	0.1374
$CaC_2O_4.H_2O$	CaO	0.3838
Fe	Fe_2O_3	1.430
Fe	FeO	1.286
FeO	Fe_2O_3	1.111
$Mg_2P_2O_7$	MgO	0.3623
$Mg_2P_2O_7$	P	0.2783
P	P_2O_5	2.2914
WO_3	W	0.7930
ZnS	Zn	0.6709
ZnS	ZnO	0.8351
Mn	MnO_2	1.582
Mn	MnO	1.29
ZnO	Zn	0.8030
FeO	Fe	0.7773
Fe	S(for FeS_2)	1.145
Fe	$FePO_4$	0.1508
$BaSO_4$	SO_3	0.3430
$BaSO_4$	BaO	0.6570

2. Methods of Analysis Using X-Ray Fluorescence(XRF) Analyser

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2.1 X-RAY FLUORESCENCE SPECTROMETRY

In recent years X-ray fluorescence (XRF) technique has emerged as a most potent analytical tool in research as well as continuous production control. Hardly any other analytical technique is so universally suited for qualitative as well as quantitative determination as the XRF analysis.

In modern X-ray fluorescence analysis sample is irradiated by polychromatic radiation from a x-ray tube. In this process, elements in the sample are excited to emit their characteristic x-ray radiations. The secondary (fluorescence) radiation consists of several lines, which are diffracted by a crystal (analyzing crystal) and separated into individual wavelengths in wavelength dispersive XRF spectrometer. In energy dipersive XRF spectrometer the quality and quantity of the radiation is simultaneously measured by a special type detector such PIN-Si and Si-Li detectors.

In qualitative analysis, X-ray fluorescence analysis has proved to be a very versatile tool. An X-ray scan requires less than two hours to identify the element present in an unknown sample in WDXRF and few minutes in EDXRF.

In quantitative analysis not only the wavelength but also the intensity of emitted radiation has to be measured, larger the relative intensity of the radiation higher is the content of respective element in the sample. For accurate quantitative analysis matching standards (mineralogical/structural match) are used to establish the relationship between the concentration and the fluorescent intensity. The relation is not very linear.Due to the interference of various elements; it may reduce or enhance the intensity of an element under examination. Thus, a good linear relationship between fluorescent radiation and concentration is not possible unless the inter-element correction is incorporated for correcting the fluorescent yield of the element under examination.

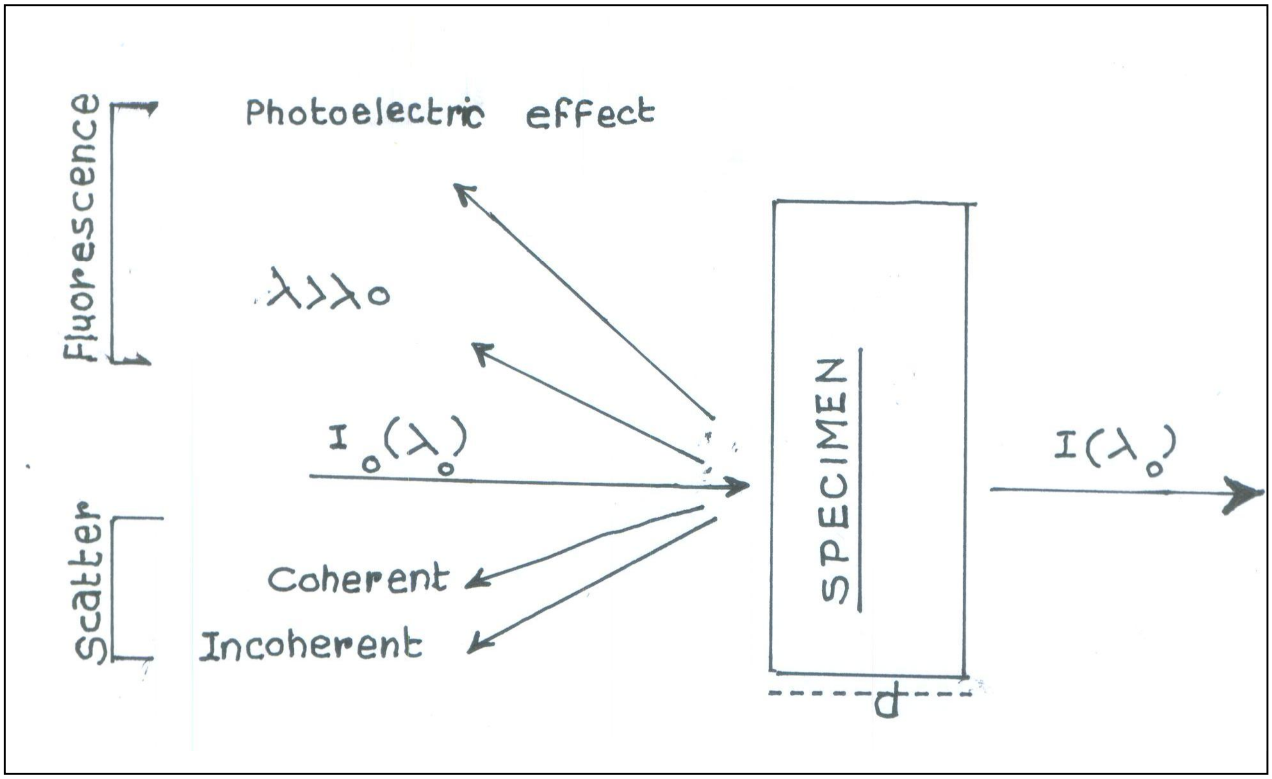
X-ray fluorescence technique is suitable to analyse as low as a few parts per million (ppm) to 100%. Pre-concentration technique helps to handle samples in parts per billion concentration. Now the commercially available instruments can analyse all elements from lithium to plutonium. This technique can analyse solid as well as liquids**.**

X-ray fluorescence technique is very useful for elemental analysis and is becoming popular with it qualities of simplicity, utility, versatility, flexibility reproducibility, speed accuracy and reliability.

Interaction of X-rays with matter

When a specimen is irradiated with X-rays the following interaction takes place and the remainder of x-rays emerges out.

(a) Absorption
(b) Ionization, photoelectric effect
(c) Scatter
(d) Diffraction



All these effects take place at the same time.

a. Absorption : In case of absorption Lambert’s Law is obeyed and then.

$$I = I_o e^{-\mu \rho d}$$

Where I_o = Incident X-ray
I = Emergent X-rays
μ = Mass absorption coefficient
ρ = Density
d = Thickness of absorber

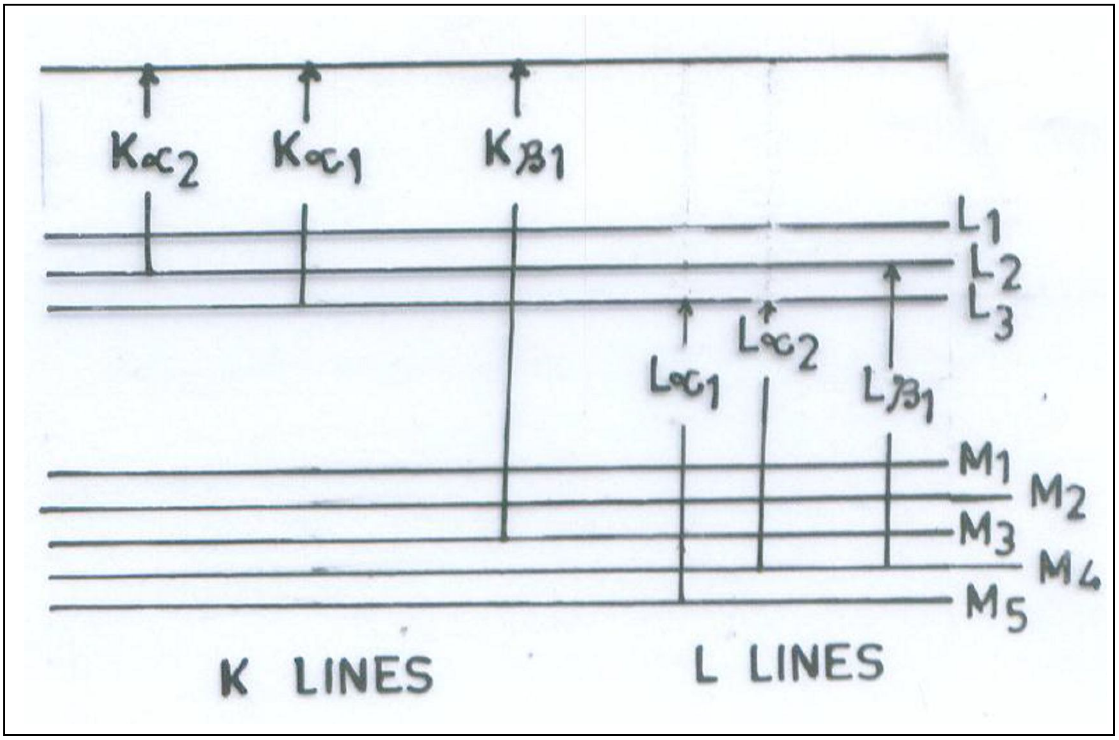
Mass absorption co-efficient is dependent on wavelength and atomic number of the element.

a. **Ionization, photoelectric effect**: Ionization is a process where an electron is removed from, or added to, the electronic cloud of an atom. X-ray photons are capable of entering the inner orbit of an atom and eject out an electron due to its impact. In this process the electron is removed from K, L or M orbit, and this gap is immediately filled by an electron from the adjoining orbit. During the process of filling up of vacancy of the electron which is in the higher energy orbit, it losses its excess energy in the form of electromagnetic radiation. As the energy difference between the two orbits of an atom is always constant, hence the radiation given out, which corresponds to the energy difference, will also be same. Therefore, this radiation becomes a primary characteristic of an atom. The loss of energy and it conversion into its characteristic radiation is given by the equation.

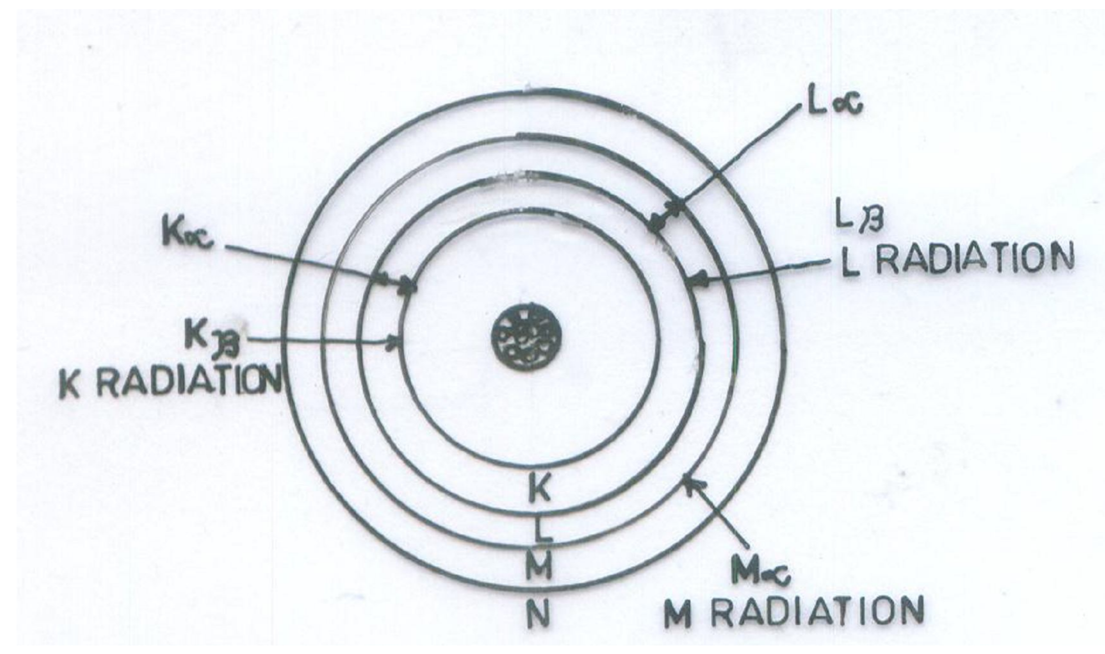
$$\Delta E = (E\text{-}E_1)\, h\nu$$

Where $E - E_1$ = the energy difference
h = Planck's constant
ν = Frequency of radiation given out.

The reason for several spectral lines from an element is due to filling up of the vacancy by an electron from one of the higher orbits according to certain selection rules.



The two major emission spectra are distinguished namely, the K spectrum (or K series) and the L-spectrum (or L series). These spectra are named, respectively, after K and L orbits. An element emits K spectrum when it s K orbit is excited. The K spectrum has two major lines K_α and K_β. The L spectrum has two major lines L_α and L_β and series of several other lines which are detected when the heavier element, which gives L lines is in major quantity. The probability diagram below gives a picture of radiation likely to be named and sources of its occurrence.



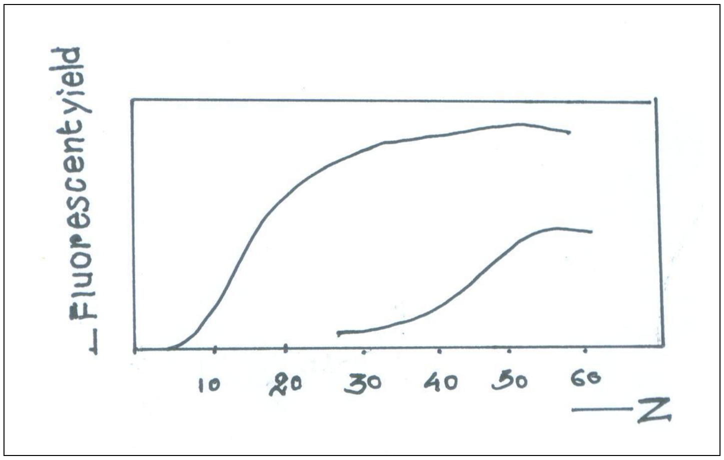
K_α and L_α lines are more intense than their respective K_β and L_β lines. They also bear a constant ratio between themselves, i.e.

$$\frac{K_\alpha}{K_\beta} = \text{constant or}$$

$$\frac{L_\alpha}{L_\beta} = \text{constant}$$

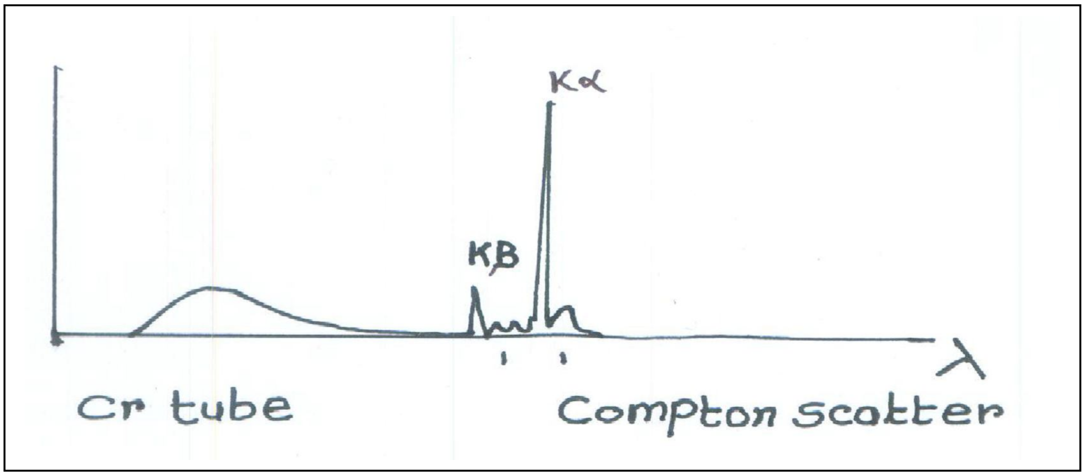
The fluorescent yield depends on the intensity of primary X-rays, which are striking the sample and the atomic number. Maximum fluorescent yield for a particular element can be obtained by proper choice of kVmA setting, is discussed in the following paragraph.

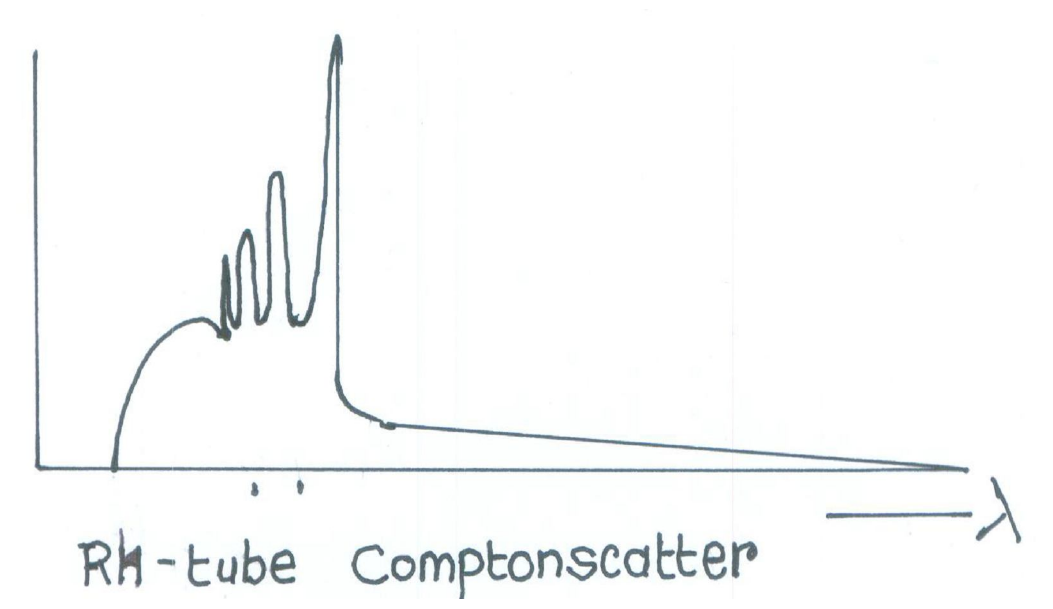
The relative fluorescent yield for the same intensity of incident X-rays is given below:



b. **Scatter** : It should be noted that no mention has been made of continuous spectrum emitted by fluorescence. There is no continuous spectrum excited because the primary X-rays do not lose their energy in a continuous fashion analogous to deceleration of electron in X-ray production by an X-ray tube. If this is true, then, there should be discrete peak at the characteristic position but it is not so, but a continuous background intensity is present. This is due to the scatter of primary radiation by the specimen. The collision between the X-ray photons and specimen may be elastic or non-elastic, consequent to which coherent scattering (Rayleigh scatter) and incoherent scattering (Compton scatter) are observed. When the collision is elastic, there is no loss of energy and hence, the wavelength of coherent scattering will be that of incident (primary) X-rays. In case of non-elastic collision there is a slight loss of energy, mostly in the form of heat energy, hence an incoherent scattering will follow the Rayleigh scattering and wavelength of this scatter will be slightly longer than the primary incident X-rays**.**

Intensity of Compton scattering increases for shorter wavelength and decreasing mass absorption co-efficient. Therefore, in case of Cr tube the Compton scatter will be small compared with that in Rh-tube, this illustrated below :



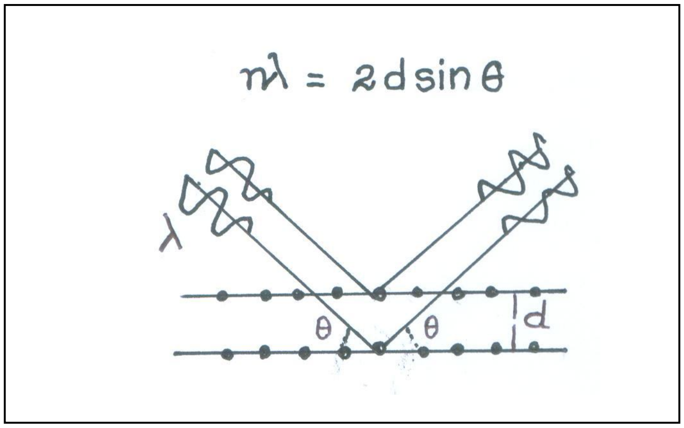


Rayleigh scatter is also recognized as tube line. Second order lines of the tube are also observed. In case of quantitative estimation, for line overlap by a tube line, other less prominent peak is used for analysis or preferably a tube where this line is free from overlap by tube line.

d. Diffraction : Diffraction is a phenomenon observed due to bending of light around an edge. In X-ray diffraction, a crystal is used for the purpose. The tiny nucleons act as an edge and subsequently the light is bent. In an X-ray diffractometer the sample is irradiated with X-rays of known wavelength and sample is observed, subsequently, ‘d’ and h,k,l, values are obtained and consequently the crystal structure of the sample is found out. An X-ray fluorescence spectrometry is exactly a reverse analytical technique where the polychromatic beam of X-ray falls on a crystal of known geometry, ‘d’ value and then, in quantitative estimation the intensity of such λ is measured. When a crystal is irradiated with a polychromatic beam of X-rays a diffraction pattern is observed. It obeys Bragg’s Law.

$$n\lambda = 2d\sin\theta$$

λ, is the wavelength.
d, is the interplainer space,
θ, is the Bragg’s angle
n, is the order of spectrum



In qualitative estimation wavelength ‘λ’ is found out.

In X-ray fluorescence technique first order spectrum is used. Hence, n will be equal to one. Then

$$\lambda = 2d\text{Sin}\theta$$

In the above equation, if any of the two parameters is known then the unknown can be calculated.

In quantitative X-ray fluorescence technique angle ‘θ‘ is used for setting a gonimeter and then to measure the intensity (I) of the radiation**.**

Resolution in case of EDXRF

In an EDXRF the X-ray detector itself acts as the depressive agent. The detector is generally a lithium drifted silicon (Si-Li) detector, which is a proportional detector of high intrinsic resolution. The resolution of the detector is typically 160-180 eV. When an X-ray photon is stopped by the Si-Li detector a cloud of ionization is generated in the form of electron-hole pairs, the number of electron-hole pairs or charge produced is proportional to the energy of X-ray photon, the charge is amplified to produce a voltage pulse that is proportional to the original X-ray photon energy.

Thus, when a range of photon energies is incident upon the detector an equivalent range of voltage pulses are produced as detector output. A multichannel analyzer (MCA) is used to sort the arising pulse to produce a histogram representation of the X-ray energy spectrum.

QUALITATIVE ESTIMATION

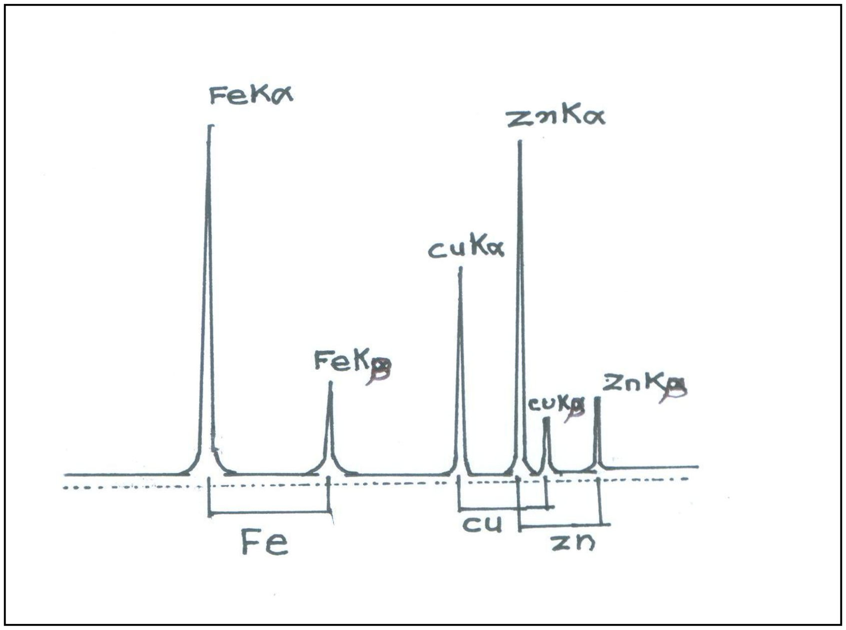
Qualitative estimation of a geological sample by X-ray fluorescence technique is very fast and accurate. Even relative quantities of various elements present can be estimated. As the geological sample is not a discrete sample which may have elements of particular origin, so the exact presence of any element cannot be predicted. Therefore, an

X-ray fluorescence qualitative identification is of great interest. A careful study and a gradual experience help in accurate qualitative estimation. X-40 software developed by Philips, Netherlands or Uniquont is very useful for identification of various elements in simple samples such as exploration sample. These automatic recorders use K_α . K_β or L_α . L_β lines for identification of the elements present. Complex samples or concentrates pose problems to these systems. In analysis of complex samples careful observation of the scan is required and the analyst has to use his skill for it interpretation.

A simple procedure for peak identification in qualitative analysis is described below :

1. Mark tube lines and Compton scatter before identifying elemental peaks.
2. Start with highest intensity or angle of the scan and mark K_α or L_α peak with respect to its angular position about presumed element.
3. Verify the correctness of this presumed identification by presence of other peak of the same element (K_α and K_β lines L_α . L_β and L_γ lines M lines). Take into consideration the relative intensity of various lines of the same element. If these peaks are not present or the relative Intensities (after making correction for abnormalities discussed latter) are not comparable then the presumed element is absent. Repeak from step 2 to identify the peak with a different presumed element. The probable associations in geological samples, ore dressing products and concentrates should also be taken into account for the above purpose.
4. If the identification is positive, mark all peaks of that element in the spectrum.
5. Continue with step 2 for the next highest intensity or angle, until all peaks are identified.

A simple X-ray scan where there is no interference from other elements present will have relative K_α , K_β , L_α and L_β peaks. The intensity of K_α line is approximately four times more than that of K_β line. A simple scan of a sample containing iron, copper and zinc will appear as –



Abnormalities in the intensity of peak In interpreting a qualitative X-ray scan the following factors must be taken into account for accurate identification of the peak:

1. Source of the sample and earlier findings.
2. Line overlap by the tube line.
3. Line overlap by the line of other element.
4. Quantitative presence of heavy element.
5. Tube used (effect of target element).
6. Absorption edge of the counter gas.

Absorption co-efficient of argon as a function of wavelength. Cadmium recorded with an argon filled proportional counter, the spectrum of cadmium, the absorption edge of the counter gas is located between the K_α and $L_{\beta 1}$ lines and hence L_α line is registered less effectively than $L_{\beta 1}$ line.

Sample preparation for XRF scan

Pressed powder samples are used for XRF scan. As there is no dilution, elements present in trace level can easily be detected. Pre-concentration techniques are rarely employed to eliminate the interfering elements and elements present in large quantities. Pre-concentrations are usually accompanied with chemical changes in the sample but they do not affect the detection of element of interest.

Generally, 5 to10 gm. of sample in –300 mesh is mixed with suitable binder and then is pressed into a pellet of suitable diameter in a suitable holder (such as boric acid cup, aluminum cup, cellulose cup, etc.).

2.2 CHOICE OF INSTRUMENTAL PARAMETERS

Detection limit and accuracy of analysis depends mostly on the choice of instrumental parameters. Separation of interfering lines or analysis of two adjacent lines largely depends on the instrumental parameters. Thus, instrumental parameters are very important for a precise and accurate analysis. Choice of instrumental parameters depends on the element to be analysed, choice of spectrometer alternatives, etc. This can be illustrated in following way **:**

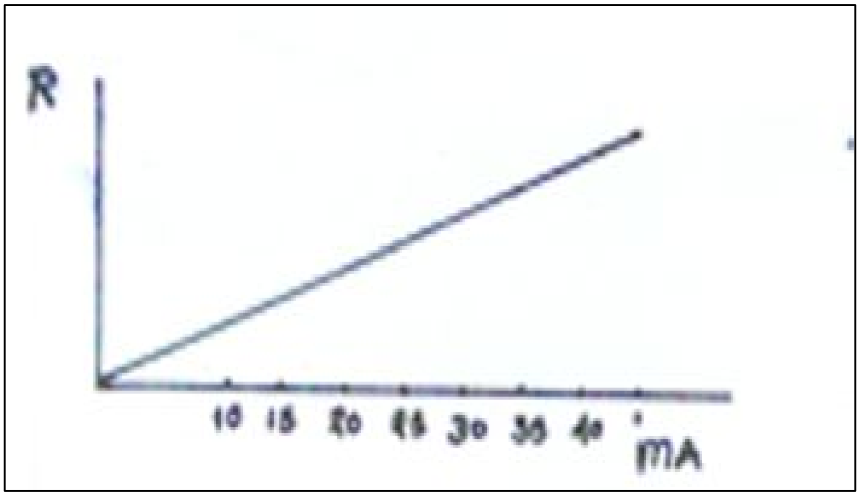
Choice of instrumental parameters

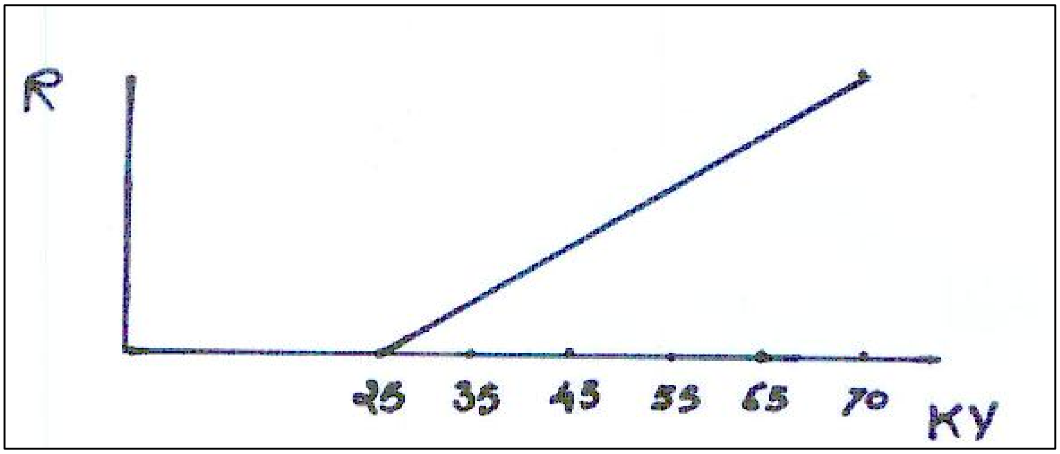
Element specific	**Application specific**	**Instrument Adjustment**
• KvmA	• X-ray tube	• Detector high voltage
• Filter	• Collimator mask	•
• Collimator	• Spectrometer medium	•
• Crystal, angle	• Flow detector window	•
• Detector	• Selection of off position	•
• Window, PHS	•	•

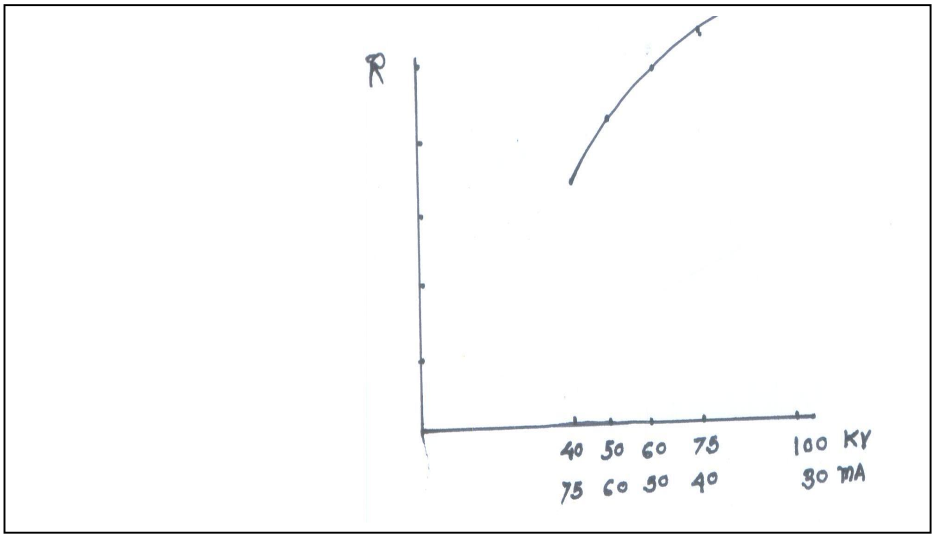
Assembling of a channel includes all above parameters. Initially a channel can be assembled as suggested by the operating manual. The ideal condition required for a particular element for a particular unit can be achieved by following the instruments operating manual.

1. **kV & mA selection** : A heavy element requires high kV and a lighter element requires high mA. Accordingly, the selection of kV/mA close to the most possible setting is first made and enter optimized in actual experiments.

Procedure : Set the channel for the element to be studied, increase mA gradually, and measure counts for each setting. In no case, the power applied should exceed the power of the tube. Now change kV by 5 units either side and repeat the observation with increasing mA setting. Find the maximum for a set of kV. mV and include this value in the channel setting







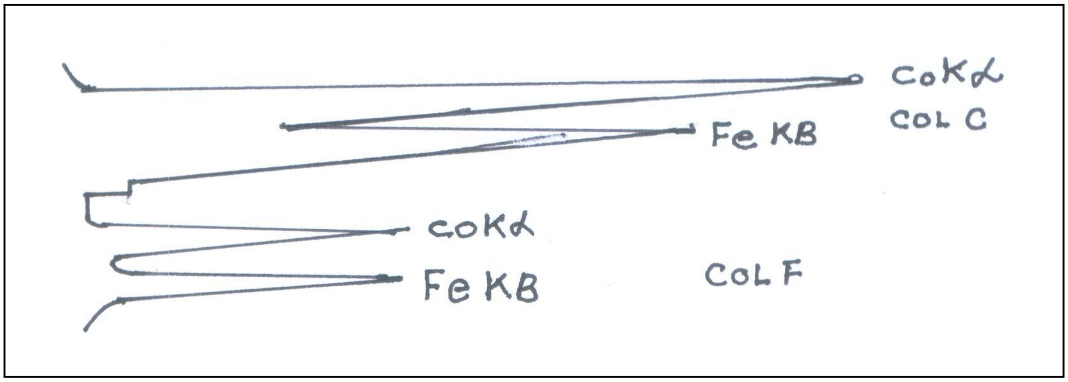
2. **Filter :** Filter selection is necessary for removal of interfering characteristic tube lines, suppression of spectral impurities from the tube spectrum and attenuation of

intensities. A filter reduces the intensity of primary X-ray and proportionally the secondary. Filter should be used only when essential.

3. Collimator : Normally, a coarse and fine collimator choice is available with the various marketed instruments. A fine collimator gives a better line separation compared to a coarse collimator, but it will yield a lower intensity. A coarse collimator can be used for lighter elements (B to Ca) and a fine collimator for heavier elements (Ti to U). This is only broad determined recommendation. Each case, however, is to be recording the spectrum of a representative sample and thus containing the collimator choice. If there is no interference from adjoining line, coarse collimator can well be used it will also considerably improve the lowest detection limit.

Collimator, serves to select a parallel beam of radiation and is used to accurately provide the angle which the resident fluorescent radiation forms with the analyzing crystal. The longer and the finer the collimator, the smaller is the divergence of the selected beam and the better is spectral resolution.

INFLUENCE OF COLLIMATOR CHOICE ON DISPERSION & INTENSITY



A fine collimator gives better separation of close lines, but yields a lower intensity. Thus, the choice of collimator depends on the nature of element and also the various interferences.

4. **Crystals & angles** : The fluorescent spectrum emitted by a sample contains lines of different wavelengths. Analysis of spectrum according to wavelength and its intensity is carried out with the aid of an analyzing crystal of known lattice parameter. The wavelength of radiation can be determined by measuring the angle of diffraction, 2θ. According to Bragg's equation.

$$n \lambda = 2d\sin\theta$$

In this equation n = 1, 2, 3 ….. represents the order of diffraction. First order diffraction is of greater interest and is generally used for analysis. Then, n = 1, and Bragg's equation reduces to.

$$n \lambda = 2d\sin\theta$$

By measuring the Bragg's angle, 'θ' for a crystal of known 'd' value, λ of the radiation measured at an angle 'θ' can easily be calculated. Now-a-days, JCPDS tables are available and hence, no calculations are needed. In latest series of instruments with JCPDS cards (computer) , the angle is automatically converted into its corresponding λ, the wavelength. The qualification of λ is of greater interest in qualitative analysis, but in quantitative determinations, the intensity of such wave length, 'λ' is measured at corresponding angle 'θ' and used for quantification of the element corresponding to the characteristic 'λ' value.

Inter-layer distance 'd' lattice parameter is much significant in respect of crystal and its capability to theoretically 'θ' can have a maximum value of 90^o, and Sin90 = 1. Thus, the Bragg's equation reduces to.

$$\lambda = 2d$$

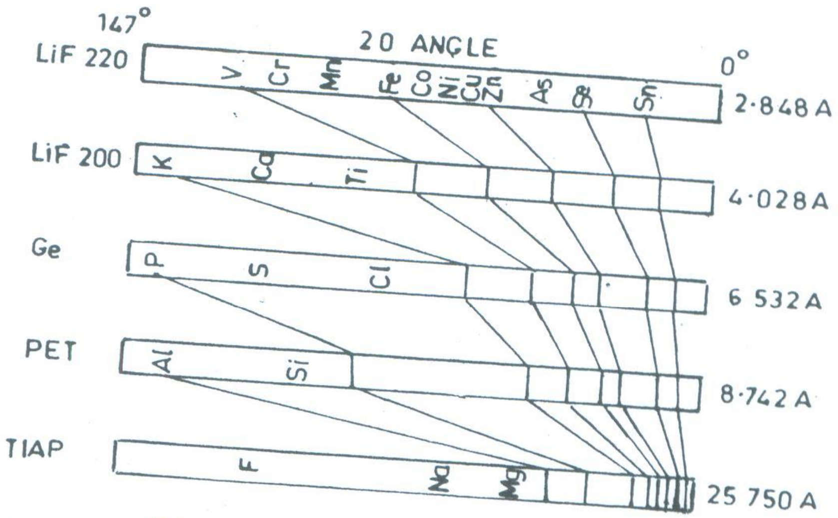
Therefore, a crystal can analyse only radiation of wavelength 'λ' shorter than '2d' or equal to '2d', which is the limit. In commercial spectrometer, the maximum angle which a gonimeter can attain is around 150^oC ($\theta = 75^o$ and Sin75 = 0.9659) and, therefore, the practical ability of any crystal will be.

$$\lambda = 2d \times 0.9659$$

$$\lambda = 1.9318\ d.$$

Therefore, ability of any crystal will be slightly less than the theoretical one. In case of crystal of larger 'd' the shorter wavelengths will be concentrated near $\theta = 0^o$, hence, they are generally used for larger wavelengths only. The crystal selection depends on the nature of the element to be analysed, consequently, the wavelength of the characteristic radiation.

The ability of crystal depressive power is illustrated in the following figure



Dispersion on various crystals

Large number of crystals with flat and curved surface are available commercially and their choice depends on user’s need. A list of commercially available crystals with their ‘d’ values and elemental range is given below:

Crystal type	**2d in nm.**	**Elemental range**
LiF420	0.180	Ni-U
Topaz	0.271	V-U
LiF220	0.285	V-U
LiF200	0.402	K-U
NaCl	0.564	-
Si	0.627	-
Ge111	0.653	P-Cl
Graphite 002	0.671	P-Cl
InSb111	0.748	Si
PE002	0.874	Al-Cl
EddT020	0.880	Al-Cl
ADP-101	1.064	Mg
T1AP-100	2.575	O-Mg
*Px-1	5.1	O-Mg
*PX-2	12.0	B-C
*PX-3	20.0	B
*PX-4	12.0	C-(N.O)

* Synthetic crystal developed by Philips, Netherlands. Similar synthetic crystals are available with the instruments manufactures by other companies.

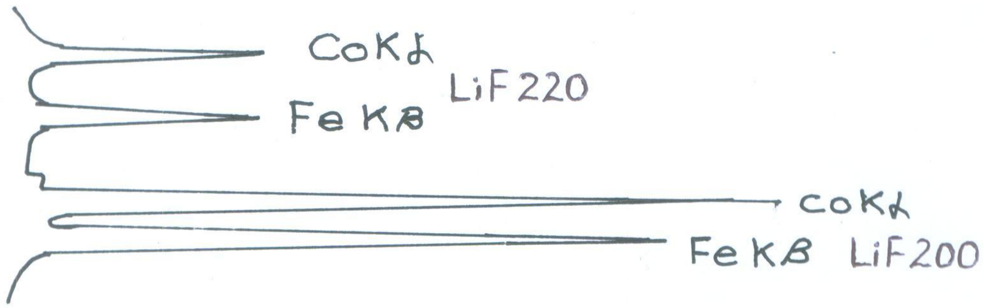
Depressive power of a crystal is inversely proportional to inter-planar distance ‘d’. Higher the inter-planar distance lowers is the depressive power and vice versa.e.g.: λ_1 and λ_2 are the characteristic wavelengths of two elements and θ_1 and θ_2 are corresponding Bragg’s angles.

Then
$$\lambda_1 = 2d\mathrm{Sin}\theta_1$$
$$\lambda_2 = 2d\mathrm{Sin}\theta_2$$

$$(\lambda_1 - \lambda_2) = 2d\,(\mathrm{Sin}\theta_1 - \mathrm{Sin}\theta_2)$$

$$\frac{\lambda_1 - \lambda_2}{2d} = \mathrm{Sin}\theta_1 - \mathrm{Sin}\theta_2$$

As Sin θ is directly proportional to θ, then the difference of Sin θ_1 and Sin θ_2, which will indirectly represent the depressive power of the crystal wavelength λ_1 and λ_2. The ratio $((\lambda_1 - \lambda_2)/d)$ will be higher for small value of ‘d’. Hence the depressive power of crystal will be higher for smaller value of ‘d’.



Reflectivity is another significant character of a crystal. It is very important for quantitative measurements and depends on the imperfections in a crystal. A truly perfect crystal would give a very low diffracted intensity because of primary extinction and would almost be of no use as an analyzing crystal. Natural and synthetic crystals vary in their imperfections. As is explained in texts on crystallography, the imperfection reduces the primary extinction and makes for far greater diffracted intensity. Higher the reflectivity greater will be the diffracted intensity. Hence, it will improve the lower detection limit. A comparison of depressive power and reflectivity of LiF220 (0.285 nm). and Li200 (0.402 nm.) is given in Figure.

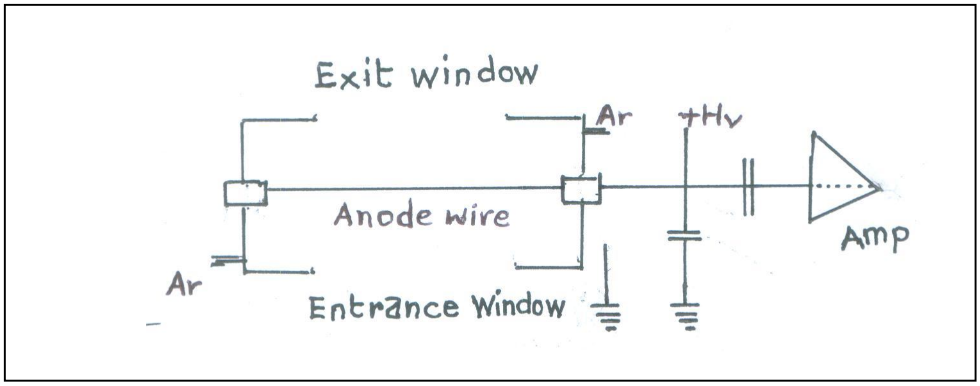
The choice of crystal depends on following three primary factors and a proper choice can be made out of available crystals on the basis of element to be analysed and its matrix (presence of other elements). (1) Element detection range, (2) Depressive power and (3) Reflectivity.

Calibration of an angle : All commercially available instruments have facilities to calibrate the angle for a particular element, which may slightly vary with the instrumental condition and setting. This can be experimentally found out and used for analysis. The angle position normally should not change with concentration but in many cases such deviation is observed. In such cases, two different angles should be used for these two different concentration range.

5. **Detectors** : Three types of counters are employed in modern X-ray fluorescence analysis, namely, proportional, flow proportional and scintillation counters.

Because of the low dead time of proportional counters, high counting rates may be recorded. The spectral sensitivity of proportional counter depends upon the wavelength and is usually limited to 0.15 to 0.23 nm.

Flow proportional counter is basically a proportional counter whose window consists of a very thin Mylar film (1 to 6μ). Thinner the Mylar film lesser will be the absorption of incident X-rays. Flow counters are useful for detection of X-rays in the range from 0.15 to 1 nm. They have very poor sensitivity below 0.05 nm. Analyzing crystal and flow detectors are normally located in vacuum in order to reduce strong absorption in air of the long wavelength radiation.



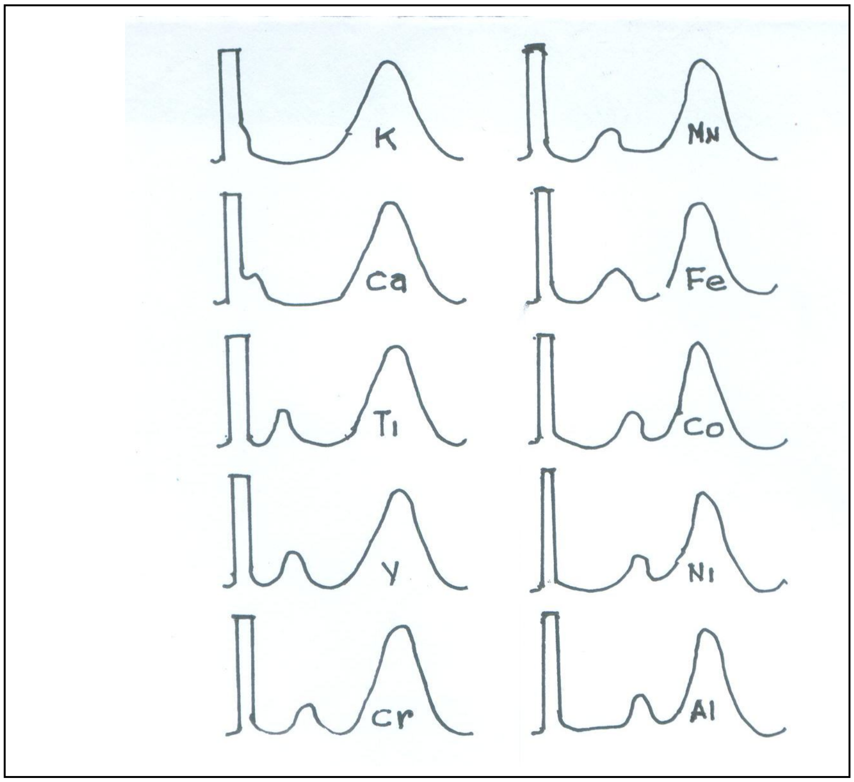
Scintillation counters have almost 100% theoretical sensitivity for all the X-ray wavelengths. For the range from say 0.2 nm. and shorter they attain almost their theoretical sensitivity. For longer wavelength, they are limited because of hygroscopic nature of NaI which is the most common crystal presently used.

Solid state detectors have also appeared on the horizon of detection. Instruments are now available with Si-Li detectors. These detectors need liquid nitrogen for storage and because of this requirement they could not yet replace the conventional counters in

WDXRF spectrometers. Their sensitivity and response are better than the above other counters.

L.S. Birks has recently developed HgI_2 detectors as X-ray detector for low energy radiation. No commercial instrument is available with this new type of detector. The flow counter is efficient for low energy radiation (<9KeV) and the scintillation counter for high energy radiation (>9KeV). For longer fluorescent radiation, flow counter is normally recommended for middle range a combination of two can be used but for shorter wavelength the scintillation counter is most suited.

6. **Window – Pulse Height Distribution** : Amplitude of electrical pulse obtained from proportional, flow proportional and scintillation counters are proportional to the energies of the absorbed photons. Pulse height distribution of radiation may easily be experimentally determined. Only a narrow range of pulse height is allowed to enter the counting electronics and then the position of window is gradually varied and a graph is plotted between the intensity and window position. From the graph the position of window is fixed so as to include the whole wave for detection. There is a phenomenon observed in case of flow-counter, for pulse height distribution curve known as escape peak. Relative position of escape peak depends on atomic number of element. When the energy of the entering X-ray is high enough, it may knock out one of the K electrons of the noble gas rather than just ionize the atoms. When this happens, a K series X-ray quantum of noble gas is emitted and, because the gas is quite transparent to its own radiation, this emitted X-ray quantum must be subtracted from that of original X-ray quantum and thus, the amplitude of that particular pulse is reduced. For practical purposes the escape peak is included in determination. Thus, the window position should be fixed in such a way so as to include the escape peak.



7. **X-ray tube** : The ability of an X-ray tube to excite fluorescent radiation depends on the position of the emitted wavelength relative to the absorption edge of the elements contained in a sample. The tube radiation consists of K and L lines that are characteristic of the anode material employed. The wavelengths and the intensities of emission must be considered in determining the choice of tube for a given application.

Performance of some of the commercially available tubes is discussed below:

1. **Chromium** : A general purpose tube with good light element capability also suitable for some heavy elements. For sample containing chromium this tube can be used with the insertion of a primary X-ray filter.

2. **Scandium** : This tube gives optimal excitation of atomic number below 21 (Sc). Preferable to chromium tube where chromium and manganese need to be determined. Gives comparable performance for heavy elements. Can be used to take over the general role of chromium tube.

3. **Rhodium tube** : Another useful general purpose fully programmable tube, combining good light element performance with high sensitivity for heavy elements.

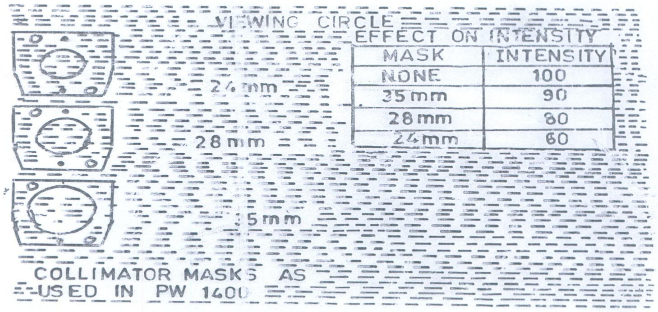
4. **Molybdenum tube** : Useful for heavy elements and specially suitable for rubidium, strontium, yttrium, uranium, thorium and the rare earth elements.

5. **Gold and tungsten** : These two tubes are for measurement of heavy elements from atomic numbers 43 (technetium) to 71 (lutetium) and also for specific excitation, such as, gold tube for Cu and Zn and tungsten for Fe and Ni.

6. **Silver** : Exhibits sensitivity comparable to rhodium tube for heavy elements. Offers a useful alternative for elements where rhodium causes spectral interferences.

7. **Dual Anode tubes** : A significant break-through was the introduction of dual anode tubes (DAT). It comprises a layer of chromium deposited on a gold substrate or scandium on a molybdenum substrate. At low kV, DATs functions as a conventional chromium or scandium tubes. But at higher voltage, radiation produced from the under laying anode materials gives most efficient excitation of heavy elements. This enables a single X-ray source to be used without any compromise over a very broad atomic number range.

7. **Collimator mask** : Collimator mask, a metallic cover on the entrance of the collimator, is a small opening. It cuts the radiation given by the collar of the holder or from the sample mount (used for small diameter samples). It reduces the intensity of secondary radiation entering the collimator. Different opening masks in sets are commercially available.



EFFECT ON INTENSITY

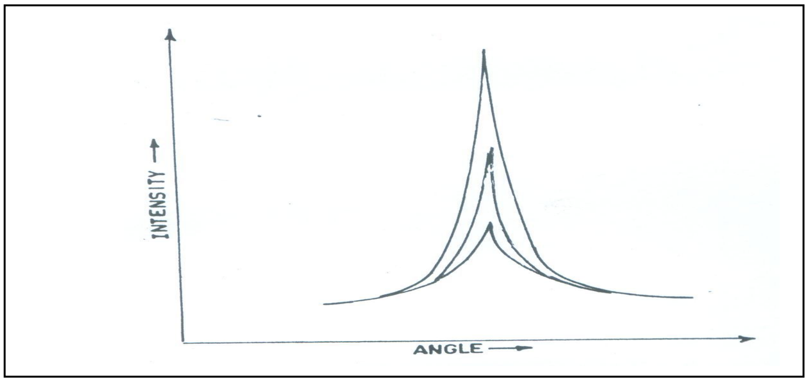
MASK	INTENSITY
NONE	100
35 mm	90
28 mm	80
24 mm	60

In many commercial instruments a choice of mask is possible**.**

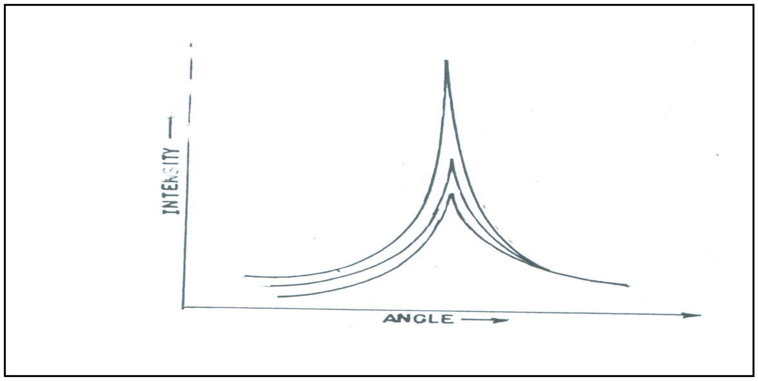
9. **Spectrometer medium** : Crystals and flow-detector are placed inside the vacuum chamber and scintillation detector is mounted in open. Heavy elements (with fluorescent radiation shorter than 2 nm.) can be analysed in air and lighter elements should be analysed in vacuum. Solids are generally analysed in vacuum. A helium medium is used for analyzing liquids. A high vacuum improves the lower detection limit of the analysis, especially for lighter elements.

10. **Flow detector window** : At the entrance (for X-rays) of flow-detector a polypropyline film/Mylar's film is fitted. Films of various thickness are available commercially. Thinner the film greater will be the chances of its rupture due to the gas pressure inside and vacuum outside, and hence, frequent replacement will be required. 6 micron window is suitable for medium and heavy elements, and 1 or 2 micron window for lighter elements.

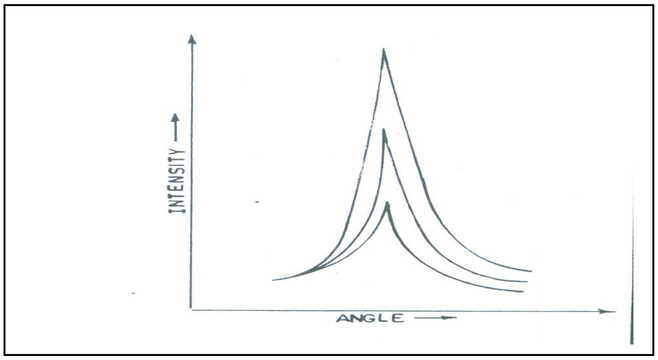
11. Selection of off position : Selection of the off-position is very important for .better and accurate analysis of an element. The rise and fall of intensity of any wavelength may be gradual or sudden. This rise and fall gives an idea regarding off selection. This can be experimentally found out by tracing the scan of the particular element for different concentration on the same position on the chart recorder for small range of angle ‘θ’. This is explained in the figures given below:



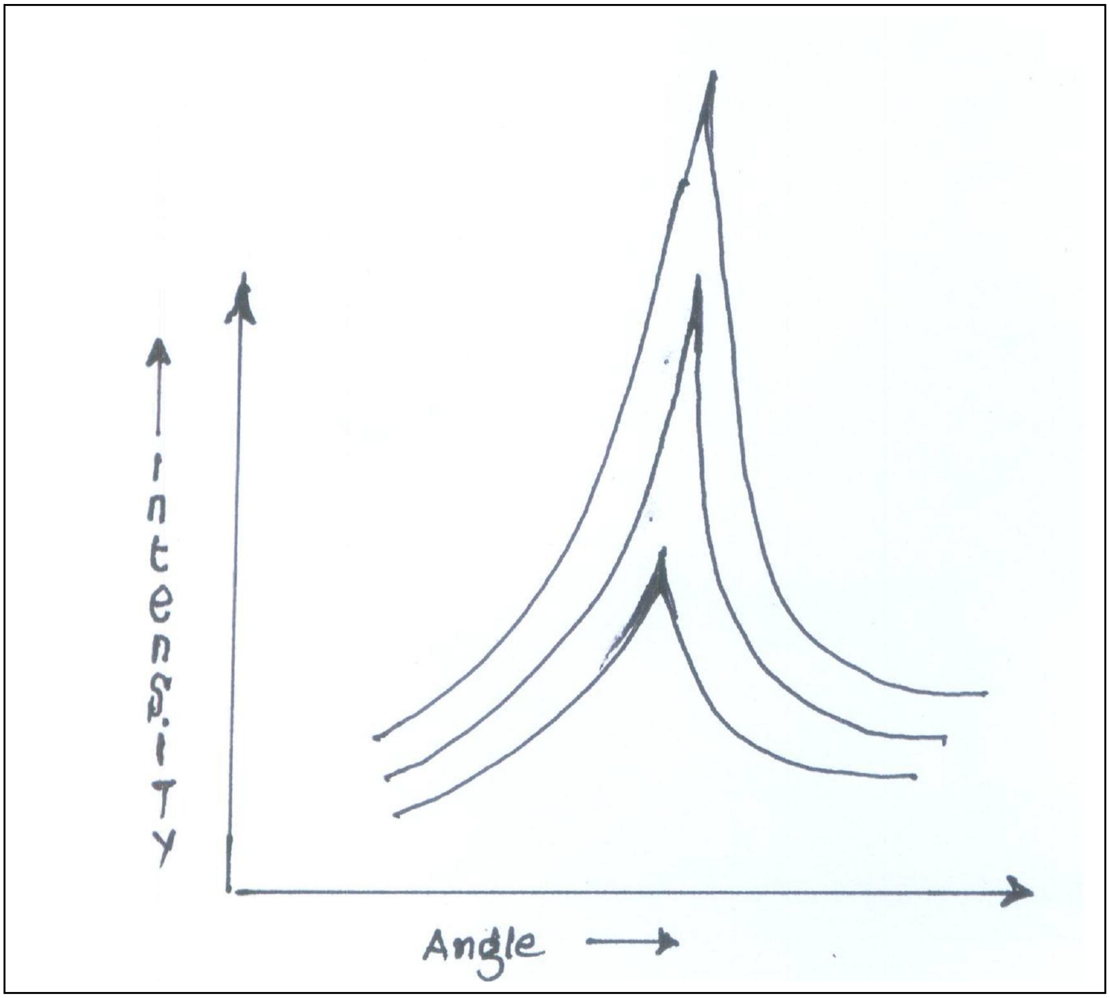
Rise and fall is gradual,
Hence, no off correction is required



Rise is not gradual, hence, negative off position
can be selected at a suitable position



Here rise is gradual but fall is not gradual,
Hence, a positive off can be selected at a suitable position



Here neither rise nor fall is gradual,
Hence, a positive and negative off should be selected at suitable position

12. Detector high voltage selection : Adjust the detector high voltage so that the maximum position of the pulse height distribution occurs at 50%. Procedure for high voltage selection is normally given in one operation manual. The maximum voltage, which can safely be applied must not be exceeded, otherwise, it may damage the electronics or the detector. A general procedure for selection of detector which voltage is,

1. Select window 49 to 51
2. Adjust high voltage to obtain the highest possible reading on the slip-chart recorder.
3. Select normal window setting by PHD.

2.3 SAMPLE PREPRATION TECHNIQUE

Claisse, as early as in 1956, traced the importance of breaking of matrix for accurate XRF analysis. Simple pressed powder pellets may lead to inaccurate determination. But, where the product produced is consistent and similar then, simple pressed powder technique is most suited due to its speed and simplicity. The choice of sample preparation technique is rather more an art than a science. A careful study on many aspects of the sample to be analysed may suggest some methods for analysis. Out of these methods, the suitable one for a particular type of analysis can be chosen experimentally.

Analysis of ores, minerals and especially ore dressing products by XRF is indeed a challenging one. Ores, minerals and ore dressing products have a variety of elements and radicals, which interfere with one another during XRF analysis. Moreover, no two ores are alike. The work of an X-ray analyst is, thus, exacting, interesting, challenging and at time tedious. But once he acquires mastery over the sample preparation technique his work becomes most simple. As far as instrumental ability is concerned it is fixed and optimal (even maximum) can be set by experiments and it will not deviate from design and manufacture. Therefore, the sample preparation technique is the cornerstone of XRF analysis. Once it is mastered, the XRF analysis is simple and easy. And if this task is not accomplished the XRF unit becomes a white elephant. Therefore, it is necessary that a sample preparation technique should be chosen for a given requirement only after careful observation and experimentation.

The producibility of the method selected for sample preparation must be sufficiently good. This means, that the error due to sample preparation must be smaller than the acceptable total analysis error. Therefore, it is recommended that even the simplest method of sample preparation should be tested for its reproducibility. Only then one should start preparing the (expensive) calibration standards.

In the following paragraphs sample preparation techniques for ores, minerals and ore dressing products are discussed. Other materials are either excluded from the discussion or are cursorily dealt like metals, alloys, etc.

There are many sample preparation techniques, which are employed for analysis of ore, minerals and ore dressing products. Most important among these are listed below and discussed in detail in the following paragraphs.

1. Freshly cut rock by diamond saw.
2. Pressed powder pellets.
3. Glass beads.
4. Solvent extraction.
5. Ion exchange.
6. Solvent impregnated papers.
7. Fire assay beads.
8. Co-precipitation and cementing.

Freshly cut rock or fresh powder pellets of powdered rock do not change the mineralogical composition of the rock. Sample preparation and analysis is very fast by this procedure. However, its drawback, render it unsuitable for accurate analysis in many cases. Pressed powdered pellets of solid solutions, glass beads, solvent extraction, ion exchange, solvent impregnated papers and fire assay beads are those techniques where the matrix of the sample to be analysed is broken with the action of suitable chemicals and converted into a matrix where the matrix effect will be considerably reduced**.**

The advantage and disadvantage of all these techniques mentioned above are discussed in following paragraphs**.**

1. Freshly cut rock : This sample preparation technique is mostly used for qualitative estimation, semi-quantitative analysis is also possible. In this technique rock is cut into a piece of suitable size and then analysed. Therefore, this technique can be employed at mine site. If the rock matrix is more or less similar reliable quantitative results are obtained. This technique requires minimum time as compared to other techniques of sample preparation, and can be employed for analysis of metals and alloys**.**

2. Pressed powdered pellets : A popular and widely employed technique in XRF analysis can be categorized broadly into two classes.

(a) Powder rock without matrix breaking
(b) Solid solution.

(a) Powdered rock is pressed into a pellet with or without binder. Finely powdered rock, less than minus 300 mesh, reduces the interferences due to grain size. If the pressed powdered pellet of powdered rock has sufficient strength then no binder is required. But where it is difficult to have good strength for a pellet without any addition then suitable binder is added to it. These binding material can further be categorized into two different categories :

Additive binders	**Non-additive binders**
Starch	Polyvinyl acetate
Boric acid	Polybutyl methacrylate, etc.
KCl	
Cellulose, etc.	

In case of additive binders a known small quantity of binder is added and mixed with known quantity of the sample and then pressed into a pellet. In case of non-additive binder a very small (negligible) quantity of binder is added to the sample and then mixed and pressed into a pellet.

Freshly cut rock, pressed powdered pellet with non-additive binder are techniques of sample preparation where no weighing is required. Hence XRF analysis involving these samples preparation techniques outweigh the other analytical techniques as in all quantitative techniques weighing is the first step of analysis. But where the matrix changes considerably, such as, ore dressing products etc., these simple pressed powdered techniques are either applicable to limited extent (lower range of concentration) or lead to inaccurate analysis. For trace analysis simple pressed powdered technique is most recommended, as the quantity of the element present is not diluted, hence detection of very low concentration is possible.

Ores and minerals analysed by pure pressed powder technique.

1. All ores for determination of trace quantities of elements.
2. Silica sand and quartz.
3. Magnesite
4. Talc
5. Soapstone

(b) Pressed powdered solid solutions emerge as the most promising sample preparation technique for its speed and accuracy in XRF analysis. Moreover, this does not suffer from problems normally faced in glass bead preparation (such as cracks and fractures, etc.). Number of fluxes can be employed for preparation of solid solution. Most important is that the melt after cooling must be stable in open for considerably long period. Hence, hygroscopic fluxes such as KOH, Na_2O_2, etc. cannot be employed for preparation of solid solutions. Some of the commonly used fluxes are listed below.

• Sodium Pyrosulphate	$Na_2S_2O_7$
• Potassium pyrosulphate	$K_2S_2O_7$
• Lithium tetraborate	$Li_2B_4O_7$
• Lithium metaborate	$LiBO_2$
• Sodium carbonate	Na_2CO_3
• Potassium carbonate	K_2CO_3
• Lithium carbonate	Li_2CO_3
• Mixture of fluxes such as	$K_2S_2O_7$ +NaF, etc.

The choice of flux should be made on the chemical nature of the sample to be analysed. The melt is carefully removed, ground to a powder and pressed into a pellet of suitable size. Normally no binder is required but where glass is formed non-additive binder such as PVA, etc. may be added. The choice of flux is most important step in solid solution analysis and is based on chemical properties of the material to be analysed. The choice of fluxes can be made as suggested below for various ores and minerals**.**

A. Potassium pyrosulphate Sodium pyrosulphate

1. Bauxite	12. Tungsten ores, & concentrates, etc.
2. Manganese ore	13. Molybdenum ores & concentrate, etc.
3. Cobalt ores	14. Vanadium ores
4. Copper ores	15. Niobium ores and concentrate, etc.
5. Iron ores	16. Tantalum ores and concentrate, etc.
6. Nickel ores	17. Tin ores and concentrate, etc.
7. Zinc ores	18. Cadmium ores
8. Indium, Thallium Gallium ores	19. Glauconite
9. Lanthanides ores, concentrates and middling	20. Corundum
10. Lead ores	21. Chromium ores
11. Titanium ores	

B. **Lithium metaborate/Lithium tetraborate**

1. Aluminium ores	9. Hafnium ores
2. Alumino silicates	10. Wollastonite
3. Clays	11. Slags
4. Chromium ores	12. Cements
5. Limestone/Dolomite/Magnesite	13. Fly ash
6. Rock phosphate	14. Soils
7. Zirconium ores	15. Silica sand/Quartz
8. Thorium ores	

C. Sodium/Potassium/Lithium carbonates :
For silicates

D. Potassium pyrosulphate with little NaF
Chromite and high refractories

3. Glass beads : Glass bead technique is a most important and popular technique for accurate analysis of various refractory samples. Non-wetting agents such as alkali halides and non-cracking agents such as sodium sulphate, etc. are normally added to obtain a good bead. Beads can be manually prepared on a blast Maker's burner, in muffle furnace, now automatic bead machines are available in market. Muffle furnace and bead machines can attain higher temperature so that the fusion is complete, the molten mass is less viscous, and can be poured easily into a casting dish. Glass beads of

30 mm or 40 mm and 2-3 mm thick are normally casted and used for XRF analysis. Glass beads of the material listed under the table 'B' on the previous page can be cast.

Loss on ignition correction is very important in this analysis. Therefore, either a calcined sample is used or the weight of the bead cast is used for correction. Loss on ignition correction, how it is employed is illustrated below:

a) Where calcined sample is used for bead preparation

Initial weight	100
Final weight	S {X = (100 – LOI%)}
Dilution factor	$\frac{X}{100}$

b) Where uncalcined sample is used for bead preparation

Initial weight	Actual wt. of the sample say A gm.
Final weight	Actual wt. of the bead, say X gm.
Dilution factor	$\frac{X}{A}$

The calibration programmes should be prepared in the similar manner and used for analysis. Commercial instruments utilizing computer software's facility allow entering dilution factor directly to correct the analysis**.**

4. Solvent Extraction : This technique is very rarely used in XRF unit.However, a very potent technique where preconcentration and elimination of other interfering material can be done. A sample is dissolved in a suitable medium, such as, acids or dissolution of fused mass in aqueous solutions and the element of interest is extracted in organic layer. This organic loaded solvent is transferred into a liquid sample cup and then measured for desired elements. Care should be taken to test the solubility of polypropylene film with the solvent to be stored in it. Alternatively the organic layer is stripped in water and then analysed. No corrosive solution should be used for analysis, as it will damage the spectrometer chamber. Alternatively, measured quantity of organic or aqueous solution is absorbed on a filter paper or pad and then dried and used for quantitative analysis.

5. Ion Exchange : Solution containing small amounts of element of interest is adsorbed on the ion exchange resins. These resins are then dried or stripped and used for quantitative analysis.

6. Solvent impregnated papers : As explained above under Solvent Extraction, a known quantity of solution is dried on a filter paper and this paper is fixed on suitable mount and then analysed. Alternatively a small tablet of filter paper is added to solution and then the solvent is evaporated. The residue is then pressed into a pellet and used for analysis.

7. **Fire Assay Beads** : Fire assay beads can be analysed for its constituents by XRF without further destruction. Fire assay technique serves as a preconcentration technique; therefore, quick and accurate analysis of these beads can be undertaken.

8. **Co-precipitation & Cementing** : The chemical process of selective co-precipitation and cementing can conveniently be employed to separate the desired ions from the solution and then these precipitates/ cements can be analysed directly or by employing fusion technique.

3. Methods of Analysis Using Atomic Absorption Spectrophotometery

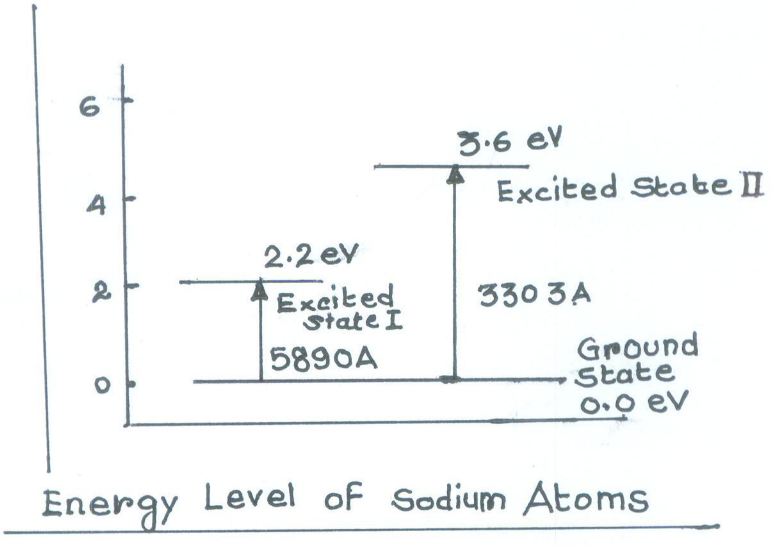
3.1 ATOMIC ABSORPTION SPECTROPHOTOMETERY

3.1.1 ATOMIC ABSORPTION

Atomic Absorption Spectrophotometry utilizes the phenomenon that atoms absorb radiation of particular wavelength.

Atoms are either in the low energy state (ground state) or in the high energy state (excited state).

The atoms in the ground state can be excited by absorbing energy from an external source. For e.g. Sodium have two levels of excited states, 2.2 eV and 3.6 eV higher than the ground state. (The unit eV reads 'electron volt' and is used to show the level of energy.) When sodium atoms in the ground state are excited by energy of 2.2 eV or 3.6eV they make transitions from the ground level to the upper level of II or I. (Fig. I) This energy is applied in the form of light. The energy differences of 2.2 eV and 3.6 eV correspond to the energy of lights having wavelength of 5890 A^0 and 3303 A^0 respectively. Sodium atoms absorb only the lights having these wavelengths. The light of any other wavelength is not absorbed at all



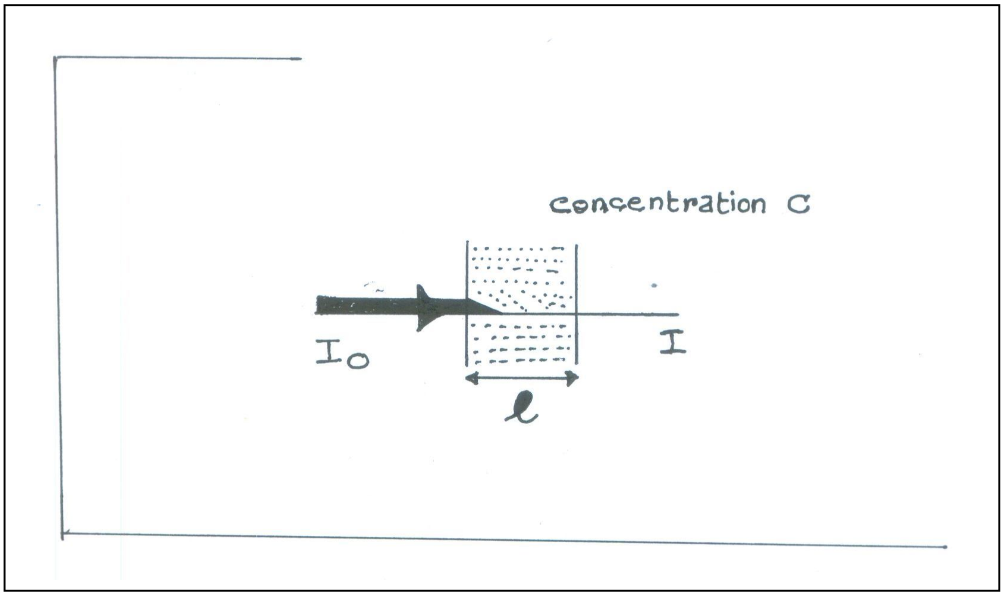
Energy Level of Sodium Atoms

Since the difference of the energy level between the ground state and the excited state is specific to each element, the wavelength of the light absorbed is decided by the element. In Atomic Absorption Spectrophotometry, hollow cathode lamps are used as the light source. They emit light of a wavelength specific to each element. Thus the concentration of the atoms of the element, under study can be calculated from the amount of the light that has been thus absorbed.

3.1.2 RELATION BETWEEN ATOMIC ABSORPTION AND CONCENTRATION.

When a light beam passes through a medium containing many atoms in the ground state, the light will be partly absorbed. The degree of absorption depends on the concentration of the atoms.

When a light of an intensity Io is made incident upon a closed medium, with a length l , which contains atoms of a concentration C , the intensity of the light will be reduced to I. The next equation holds for the relation between the I and the Io



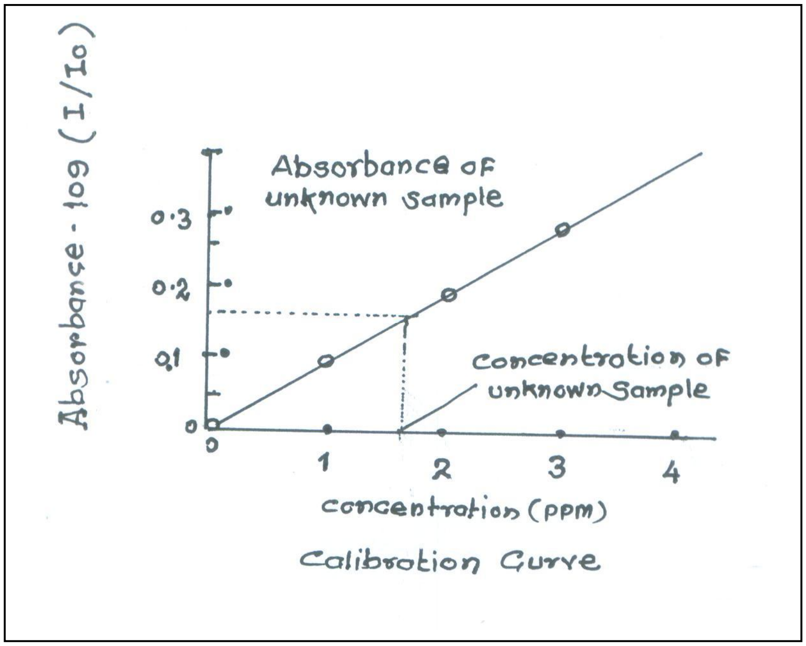
$$I = Io \times e^{-K.\,l.\,C.}$$

$$\text{Or} \quad -\log {}^{I}/_{Io} = K.\,l.\,C.$$

Where K: proportional constant

This equation is called the Lambert - Beer's Law.
The term $-\log {}^{I}/_{Io}$ is called absorbance. The equation tells us that absorbance is linearly proportional to the concentration of atoms.

When the absorbance of Standard samples the concentration of which are say 1, 2, and 3 ppm are plotted against the concentrations, a straight line as shown in Fig. will be obtained. This line is called the calibration curve for the particular element. The concentration of the element in an unknown sample can be determined from the absorbance by means of the concentration curve as shown in the following Fig.



Calibration Curve

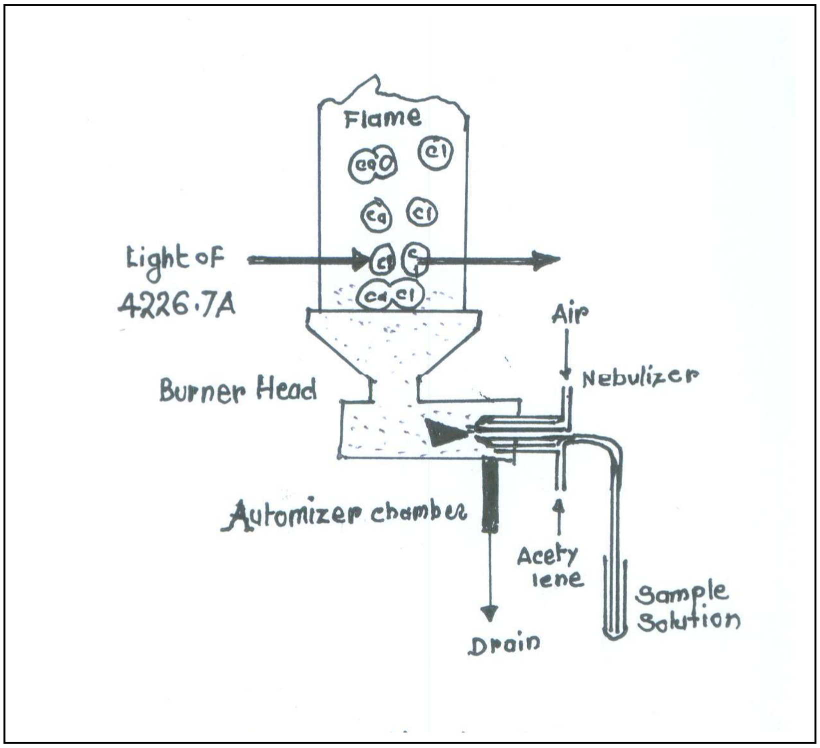
3.1.3 ATOMIZATION OF SAMPLE

The principle so far described applies only to the light absorption of “free atoms”. “Free atoms” are those atoms that are not combined with other atoms. No atoms exist in sample matrices in free state they are combined to form molecules. For e.g. Sodium atoms in seawater, are combined with chlorine atoms to form sodium chloride (NaCl) molecules. Since molecules do not absorb light, it is necessary to ‘break’ their combination to produce free sodium atoms. This process is called atomization.

The most popular method of atomization by heat – samples is heated to a high temperature, so that molecules are converted into free atoms. This method is classified into the flame method in which a chemical flame is used as the heat source, and the flameless method in which a very small electric furnace is used.

a) **Flame Atomization Method ----**

Molecules are atomized in a flame produced on a burner. The burner as shown in Fig.. In this for e.g. the object of analysis is calcium, which exists as calcium chloride in the sample solution. First, the sample is nebulized by the nebulizer. Large droplets of sample solution are exhausted as drain, and only the fine mist is fed into the flame after being mixed with fuel and support gases. In the flame, the mist is instantaneously vaporized and small particles remain in the flame. As the small particles of calcium chloride travel further through the flame, they are decomposed in to free calcium atoms. If a light beam of 4227 A^0 (wavelength for calcium) is introduced through this part of the flame, atomic absorption can be measured. If the light should pass through the upper part of the flame, where some of the calcium atoms combine with oxygen to produce calcium oxide or some are ionized, the absorption sensitivity will decrease because of the reduced amount of free calcium atoms.



Flame Atomisation

Various types of flames have been used in atomic absorption spectroscopy, and now the following four types are most commonly used, not only because of their high sensitivity but also because of the safety, ease of operation, and low cost. These four types of flames, having different temperature and gas characteristics, are selectively used for different types of elements.

Air – Acetylene (Air – C_2H_2) flame ----

This flame is most widely used. About 30 elements are analysed with this flame.

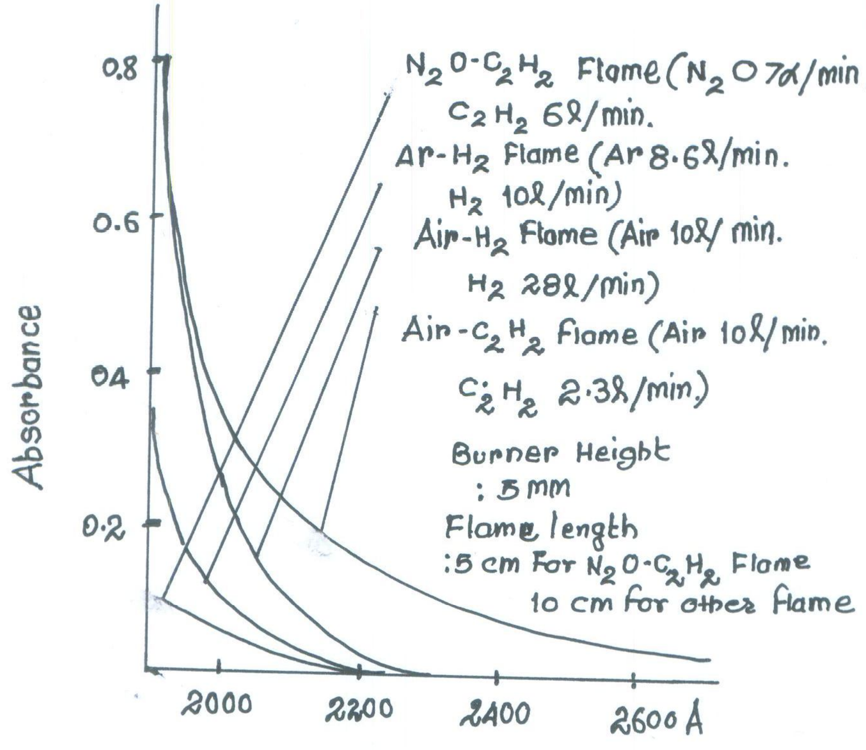
Nitrous oxide – Acetylene (N_2O – C_2H_2) flame ---

The N_2O-C_2H_2 flame provides the highest temperature of all the flames used in atomic absorption spectroscopy. Hence it is most effectively applied to analyses of – "refractory" elements like Al, V , Ti etc., which form very stable oxide molecules and are hardly atomized in lower temperature atmosphere as in air – acetylene flame.

Also, its high temperature minimizes the interferences of coexisting elements. This flame, therefore, is sometimes used in analysis of those elements which are usually analysed with an air-acetylene flame.

Air – Hydrogen (Air – H_2) flame and Argon Hydrogen (Ar – H_2) flame ---

Flames using Hydrogen as the fuel have the advantage that the absorption by the flame alone is extremely small in the short wavelength region.



Light Absorption by Various Flame

These flames, therefore, ensure lower noise level, compared with the air-acetylene flame, in analysis of such elements as As, Se, Zn, Pb, Cd and Sn in which short wavelength analytical lines are used**.**

When the analytical line is shorter than 2000A^o in analysis of As (1937 A^o) or Se (1960 A^o), it is usual to use an argon-hydrogen flame which has a still smaller absorption.

The disadvantage of hydrogen flame is that since the flame temperature is low, the interference of the co-existing elements is relatively large**.**

FLAME TEMPERATURE

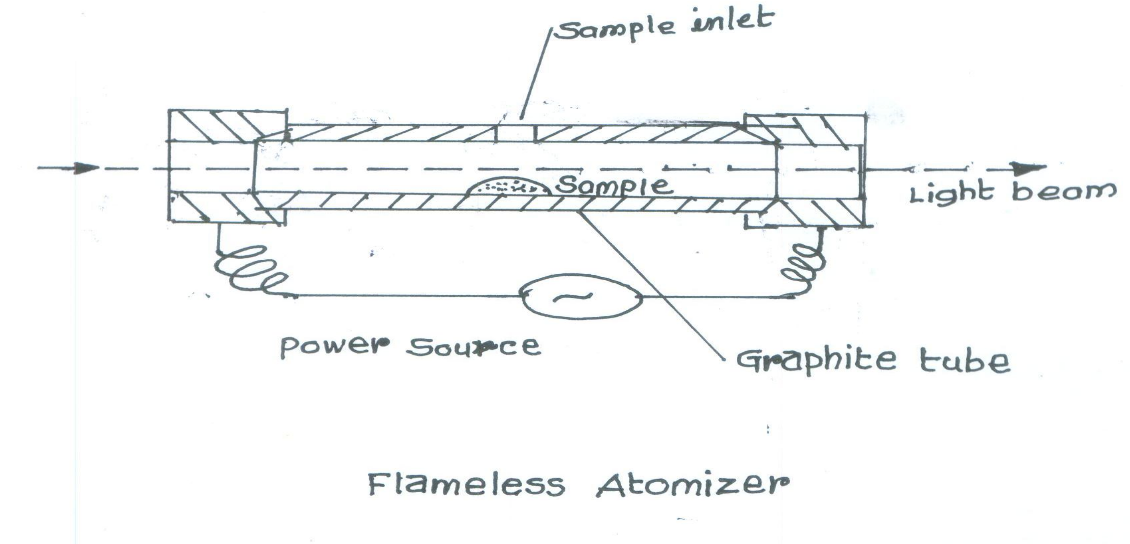
Flame	**Temperature Maximum**
Ar-H_2	1577°C
Air-N_2	2045 °C
Air-C_2H_2	2300 °C
N_2O-C_2H_2	2955 °C

Flameless Atomization Method

The flame atomization method is now used as standard method, because it ensures good repeatability and ease of operation. It has a big disadvantage that only about 10% of sample is atomized and about 90% of it is exhausted as drain. This poor atomization efficiency is claimed to be the main restriction of sensitivity given by the flame method.

The flameless atomization method has recently gained a wide popularity which consists of heated graphite tube and it ensures 10~200 times higher sensitivity than the flame atomization.

Sample is placed in a graphite tube and an electric current about 300 amperes at the maximum is allowed to flow through this tube. Thus the tube heated to a high temperature and the sample is atomized**.**



Flameless Atomizer

The temperature of the graphite tube can be freely adjusted by changing the current supplied to the tube. Thus, the optimum temperature condition can be attained required for the type of sample and the element to be determined.

Inert gas such as oxygen and nitrogen is allowed to flow through the graphite tube to purge the air to prevent oxidation loss of graphite tube.

The biggest advantage of the flameless atomization method is that since the sample injected is almost completely atomized, the sensitivity is extremely high. It is very effectively used when sample concentration is extremely low and when sample volume available is very small.

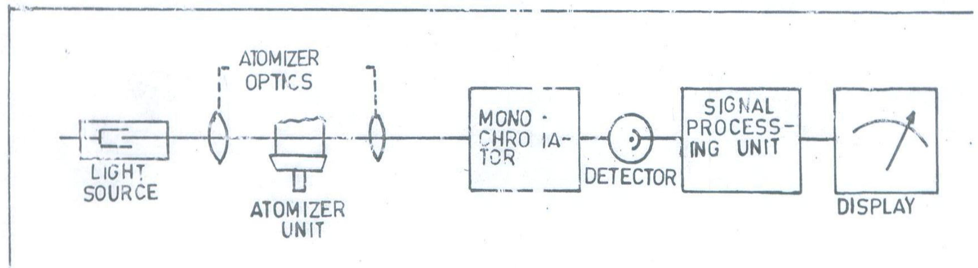
The flameless atomization method, has also some drawbacks. First, the interference of co-existing compounds is greater than in the case of flame atomization method. When the background absorption by the co-existing molecules is especially great, it is necessary to adjust the temperature and period of ashing so that the background absorption does not overlap the atomic absorption.

Next, the variation in the volume of sample injected (5~20 ml) and in the position of injection may cause variation in the photometric values. As the result, the repeatability is 3~10 times worse compared with the flame atomization method. To obtain high repeatability, it is necessary that the operator is skilled to some extent.

Construction of Atomic Absorption Spectrophotometer

An Atomic Absorption Spectrophotometer mainly consists of a light source, an atomizer, a monochromator and a detector. Besides this, the instrument required an optical system that combines these components, a processing system that converts detector signals into a form that can be easily quantitated, and a power supply.

Fig. shows a typical layout of an atomic absorption spectrophotometer.



BASIC LAYOUT OF ATOMIC ABSORPTION SPECTROPHOTOMETER

An Atomic Absorption Spectrophotometer is different from other spectrophotometers in the following points.

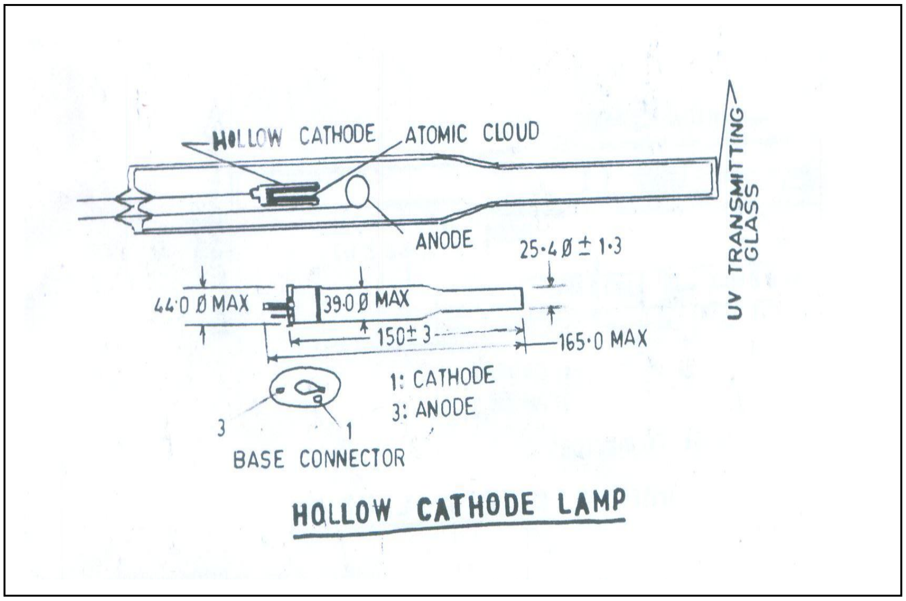
a) Atomic Absorption occurs only at the wavelength, which is strictly specific to the element under study with the slightest shift in the wavelength, the atomic absorption will cease to occur. In A.A.S., it is necessary to use a light source that emits a line spectrum, the wavelength of which exactly coincides with that of the element under study. The light source is called ‘Hollow Cathode Lamp’.

If a deuterium lamp, which emits wide wavelength light, should be used in atomic absorption, a very expensive, high-resolution monochromator would become necessary in order to isolate a 1/100 angstrom wide radiation. Even if this is accomplished, the sensitivity and accuracy obtained would be inferior to those provided by a hollow cathode lamp,.

b) Very intense light is emitted from the flame or the graphite furnace in the atomizer. If this light should directly hit the detector, the detector may be broken or its accuracy may be greatly lowered. To prevent this trouble, a monochromator is placed between the atomizer and detector, so that most of the light from the atomizer is kept away from the detector.

Light Source Unit

The light source unit for an Atomic Absorption Spectrophotometer consists of Hollow Cathode Lamp and its holder and a power supply.



A Hollow Cathode Lamp and an anode are enclosed in a glass tube, which is filled with neon or argon gas of around 10 Torr. in pressure. The Cathode is made of the element to be measured or its alloy.

Deuterium Lamp for Automatic Background Correction

A deuterium lamp is generally used for automatic background absorption. Deuterium lamps are available in two types of, hot – cathode type and cold – cathode type.

A cold cathode type deuterium lamp has the same construction as an ordinary hollow cathode lamp. It encloses deuterium gas and is turned on by the same power supply as that for a hollow cathode lamp.

A Hot Cathode type Deuterium Lamp, which is used as the UV light source of a UV- VIS spectrophotometer, is turned on by a power supply having a capacity of 300 milliamperes.

A hot – cathode type deuterium lamp, by contrast provides highly intense light, and moreover, its light is well balanced with the light of hollow cathode lamps. The influence of noise is much reduced. It can be used in the range up to 4300 A^o

For all reasons, hot cathode lamps are very widely used for automatic correction of background absorption.

2 Atomizer Unit (Burner and Gas Controller)

Burner -- The flame atomization method is more popular than the flameless atomization method. All atomic absorption spectrophotometers are equipped with a burner as standard.

There are two types of burners, premix type laminar flow burner and total consumption burner.

Premix Type Laminar Flow Burner –

This burner is used for air – acetylene, nitrous oxide – acetylene, air – hydrogen and argon – hydrogen flame. A Laminar flame is given out of a slot, 0.5 mm wide and 50 mm or 100 mm long, on the burner head.

The nebulizer is a precision sprayer which takes up sample solution through the capillary and feeds it into the atomizer chamber as a fine mist. In the atomizer chamber, a glass bead (disperser) is placed near the outlet of the nebulizer, so that the mist collides with it at a great speed to be further dispersed into finer mist. The large drops produced in the atomizer chamber are exhausted as drain.

The mist is mixed with acetylene and air and fed to the flame on burner head.

Samples of atomic absorption spectrophotometry often contain strong acids or alkalies, so the burner, and especially the nebulizer, must be corrosion resistant.

The burner head has a slot, 5cm long or 10cm long. The 5cm- long slot burner head is used for nitrous oxide- acetylene flame, and the 10cm-long slot burner head for the other three flames. The 10cm slot burner head can not be used for nitrous oxide-acetylene flame since it may cause a flash-back due to a very high combustion speed of this gas mixture**.**

It is necessary that the position of burner head can be adjusted vertically and horizontally, so that the light will pass the part of the flame where the excited atoms are most concentrated. It is possible to lower the sensitivity by rotating the burner head to shorten the path length in the flame that the light travels.

Total Consumption Burner

The total consumption burner produces a cylindrical flame of hydrogen gas. The sample solution is aspirated by air and directly sprayed into the center of the flame. The name, “total consumption” means that it uses total volume of the solution aspirated through the capillary.

Although it is useful for a viscous sample, the total consumption burner is not used frequently because of its high audible noise and its lower sensitivity than the premix burner.

Gas Controller

This unit selects and controls the flow rates of the fuel gas (acetylene or hydrogen) and the support gas (air nitrous oxide or argon).

3.2 SAMPLE PREPARATION FOR AAS

Weigh about 0.1 to 0.5 g sample (dry or roasted where necessary) in a 250 ml beaker. Add about 10-15 ml aqua regia (AR) and digest the sample for half an hour, add 4 to 5 drops of HF and then dehydrate slowly to dryness and finally dissolve the dried mass in nitric acid. Dilute it with a little water and filter it with Whatman paper No.40 in 100 ml flask, make up the volume to 100 ml with distilled water.

Aspirate the solution to AAS. Dilute the solution if required.

Lead

For higher concentration of lead, after dissolution of dried mass in nitric acid (AR) add a pinch of tartaric acid and 10 ml of saturated solution of ammonium acetate and boil it for 10 minutes and filter and make up.

Manganese

For manganese ore sample preparation should be in HCl (AR).

Cesium

For cesium weigh about 0.1 g of sample in 100 ml Teflon beaker and treat it with aqua regia 15-20 ml on hot plate. Cover with watch glass for some time. After removing watch glass and when red fumes ceases add 2-5 ml HF and 2 ml perchloric acid. Heat it to dryness and extract in diluted HNO_3 and filter with Whatman filter paper No.40. Make up (after adding KCl to have final concentration of solution to 2 mg/ml of K) to 100 ml. in 100 ml plastic volumetric flask and aspirate it to AAS.

Silver

For silver, weigh about 0.5 g of sample in a graduated digestion tube; add 10 ml of aqua-regia. Digest it on hot plate and keep it for overnight. Add 10 ml diluted ammonia (1:1) slowly, cool it in ice cold water, and add little excess. Dilute it to nearest volume shake well and allow ppt to settle for 1 to 1 ½ hours and aspirate the supernatant solution to AAS.

Gold

For gold weigh about 10 g of sample (sulphide ore) in silica petridish. Roast in furnace at 640°C for 1 hour. Transfer the cooled mass in a 250 ml glass beaker add 50 ml aqua regia and digest and dehydrate. Add 20 ml HCl (AR) and dry. Repeat twice-thrice to remove nitrate ions. Add 20 ml of HCl and 50 ml distilled water boil and filter with Whatman filter paper No.40 with pulp. Wash the residue 5-6 times with hot water. Heat filtrate to boiling to reduce volume. Add 1.5 mg of potassium tellurite (3-4 drops of saturated solution). And add 20% of stannous chloride solution till tellurium (black ppt) gets ppted. Add 2-3 drops in excess boil and cool.

Transfer the entire solution with ppt in a separating funnel. Add 10 ml toluene shake well. Allow to settle and discard the aqueous layer. Wash solution with 2N HCl twice-thrice. Add 3 ml of 1:4 HBr solution and 2 ml 1%$KBrO_3$ solution shake and allow to settle.

Element (Hollow Cathode Lamp)	Wavelength (nm)	Flame Type
Ag	328.1	Air/Acetylene
Au	242.8	Air/Acetylene
Bi	223.1	Air/Acetylene
Cd	228.8	Air/Acetylene
Co	240.7	Air/Acetylene
Cs	852.1	Air/Acetylene
Cu	324.7	Air/Acetylene
Fe	248.3	Air/Acetylene
Mn	279.5	Air/Acetylene
Ni	232.0	Air/Acetylene
Pb	217.0	Air/Acetylene
Rb	780.0	Air/Acetylene
Zn	213.9	Air/Acetylene
Al	396.2	N_2O/acetylene
Ba	553.6	N_2O/acetylene
Cr	357.9	N_2O/acetylene
Ga	403.3	N_2O/acetylene
Ge	265.1	N_2O/acetylene
Mo	313.3	N_2O/acetylene
Se	196.0	N_2O/acetylene
Sn	235.5	N_2O/acetylene
Sr	460.7	N_2O/acetylene
Ti	364.3	N_2O/acetylene
V	318.4	N_2O/acetylene

Take out aqueous layer in graduated digestion tube. Make up to nearest volume and aspirate to AAS instrument

3.3 DETERMINATION OF LITHIUM IN LITHIUM, RUBIDIUM, CESIUM IN TUNGSTEN ORES, MINERALS AND BENEFICIATION PRODUCT AND MICA.

Scope

This procedure is applicable for determining the lithium in lithium rubidium cesium and tungsten ores, minerals and beneficiation product and mica by means of flame emission atomic spectrometric technique.

Principle

The sample is decomposed by acid attack involving hydrofluoric acid, perchloric acid and oxalic acid. Potassium chloride is added as ionization buffer to stabilize emission signal (kaschloride 800 mg/ml).

Reagents and standards

1. **Hydrofluoric acid AR, 40%**
2. **Hydrochloric acid AR**
3. **Perchloric acid, AR**
4. **Nitric acid AR**
5. **Oxalic acid, 1% solution –** Dissolve 1 g. of AR oxalic acid in 100 ml distilled water
6. **Potassium chloride solution**, **K-40 mg/ml –** Dissolve 7.63 g of AR potassium chloride in 100 ml distilled water.
7. **(A) Standard lithium solution – 1000 ppm** : Dissolve a slurry of 0.5323 g. lithium carbonate in 30 ml. of water by addition of 1.5 ml. Conc. hydrochloric acid. After release of carbon dioxide by swirling dilute to 100 ml.

   (B) Standard lithium solution – 100 ppm – Dilute 10 ml of (A) to 100 ml containing 2 ml conc. hydrochloric acid (Add by pipette)

   (C) Standard lithium solution – 10 ppm – Transfer 10 ml of (B) to 100 ml volumetric flask. Add 2 ml conc. hydrochloric acid by pipette and make volume to the mark by distilled water.

   (D) Standard lithium solution – 5 ppm – Transfer 50 ml. of (C) to 100 ml. volumetric flask. Add 1 ml of conc. hydrochloric acid and 2 ml. of potassium chloride using pipette and make volume to the mark by distilled water.

(E) Standard lithium solution – 2 ppm – Transfer 20 ml. of (C) to 100 ml volumetric flask. Add 1.6 ml conc. hydrochloric acid and 2 ml potassium chloride solution by pipette and make volume to the mark by distilled water.

(F) Standard lithium solution – 1 ppm – Transfer 10 ml. of (C) to 100 ml volumetric flask. Add 1.8 ml. Conc. hydrochloric acid and 2 ml potassium chloride by pipette and then make volume to the mark by distilled water.

Procedure

- Take an appropriate weight of minus 200 mesh particle size mineral sample in a clean Teflon beaker (100 ml capacity). Record the weight to the nearest 0.0001 gram (The appropriate weight of sample (Step-1) and appropriate size volumetric flask (Step-6) are dependent on the concentration of the oxide in the sample, the sensitivity of instrument used for analysis and the range of the calibration curves or standard solutions used for comparison. The suggested sample weight and final volume for mineral 0.1-0.2% lithium is 1 gram and 100 ml, respectively. For mineral samples yielding concentrations outside the working range of the calibration solutions, appropriate changes should be made in the sample size (say 0.1 gm) and /or final volume or dilution to 10, 50, 100, 500 fold volumes.
- Moisten with water; add 5 ml nitric acid, 5 ml hydrofluoric acid and 2 ml perchloric acid.
- Cautiously evaporate the solution to dryness on a hot plate (Temp. 125-150^{o}C).
- Allows the beaker to cool, add 2 ml hydrochloric acid, 10 ml oxalic acid solution and 5 ml hydro fluoric acid and warm to digest the residue, and then finally evaporate to dryness.
- Now cool the beaker, add 2 ml conc. hydrochloric acid, 2 ml potassium chloride solution and 20 ml distilled water and heat to digest residue to a clean solution.
- Filter if necessary through filter paper into the appropriate size volumetric flask washing the filter paper thoroughly.
- Cool the solution to room temperature, dilute to volume with water and mix well.
- Determine the lithium content by flame emission at operational instrument parameters given below using a flame atomic absorption spectro-photometer in emission mode.

Wavelength	670.8 nm
Slit width	0.5 nm
Instrument mode	Emission mode
Calibration parameters	1 ppm, 2 ppm and 5 ppm.

Calculation

$$\text{Li ppm} = \frac{\text{Li ppm reading x Final volume (ml)}}{\text{Weight of sample (g)}}$$

3.4 DETERMINATION OF RUBIDIUM IN LITHIUM, RUBIDIUM, CESIUM INTUNGSTEN ORES, MINERALS AND BENEFICIATION PRODUCT AND MICA.

Scope

The method is designed to estimate rubidium in lithium, rubidium, cesium and tungsten ores, minerals and beneficiation products and mica using flame emission atomic spectroscopy**.**

Principle

The sample is decomposed by acid treatment. Potassium ion (800 mg/ml) as potassium dihydrogen orthophosphate is added to the sample solution as ionization buffer to stabilize and condition the emission signal**.**

Reagents and Standards

1. **Hydrofluoric acid AR, 40%**
2. **Hydrochloric acid AR**
3. **Perchloric acid, AR**
4. **Nitric acid AR**
5. **Oxalic acid, 1% solution –** Dissolve 1 g. of AR oxalic acid in 100 ml distilled water
6. **Ionisation buffer, potassium dihydrogen ortho phosphate, potassium 40 mg/ml –** Dissolve 13.95 g of potassium dihydrogen orthophosphate in 100 ml distilled water**.**
7. **(A) Standard Rubidium solution –** 1000 ppm Rb - Dissolve 0.1415 g. rubidium chloride in 100 ml distilled water.
8. **(B**) **Standard Rubidium solution –** 100 ppm Rb – Dilute 10 ml of (A) to 100 ml by distilled water.

   (C) Standard Rubidium solution – 10 ppm Rb – Dilute 10 ml of (B) to 100 ml by distilled water.

   (D) Standard Rubidium solution – 5 ppm Rb – Add 50 ml. of (C) to 100 ml. volumetric flask. Add 2 ml of potassium buffer and 2 ml. of conc. hydro-chloric acid and dilute to 100 ml. by distilled water. Prepare fresh daily.

   (E) Standard Rubidium solution – 2 ppm Rb – Take 20 ml. of (C) to 100 ml volumetric flask. Add 2 ml potassium buffer and 2 ml. conc. hydrochloric acid. Make volume to the mark by distilled water.

   (F) **Standard Rubidium solution** – **1 ppm Rb –** Transfer 10 ml. of (C) to 100 ml volumetric flask. Add 2 ml. Potassium buffer and 2 ml con. Hydrochloric acid. Mix and make volume to the mark by distilled water.

Procedure

- Transfer to the nearest 0.0001 gram, the 0.1-1.0 of a dry (110°C for 30 minutes) minus 200 mesh mineral sample to a Teflon beaker (100 ml. Capacity).
- Moisten with distilled water; add 5 ml nitric acid, 5 ml HF and 2 ml perchloric acid.
- Place the beaker on a hot plate (Temp. 125-150°C) and evaporate to complete dryness.
- Allows the beaker to cool, add 2 ml conc. hydrochloric acid, 10 ml oxalic acid solution and 5 ml hydro fluoric acid
- Heat to digest and finally evaporate to dryness
- Add 2 ml. Conc. hydrochloric acid, 2 ml.Potassium dihydrogen orthophosphate buffer and 25 ml. distilled water. Heat to dissolve residue completely.
- Quantitatively transfer the contents of the beaker to a 100 ml. volumetric flask.
- Cool to room temperature and dilute to volume with distilled water.
- Using an atomic absorption spectrophotometer in emission mode measure the radiation for rubidium in calibration standard range.
- On higher concentration of rubidium in sample solution compared to calibration standard range dilute original solution to 10/50/100 fold stage.
- The operational parameters of instrument are as under.

Wave length	780 nm
Slit width	0.2 nm
Instrument mode	Emission mode
Calibration parameters	1 ppm, 2 ppm and 5 ppm.

Calculation

$$\text{Rb ppm} = \frac{\text{Rb ppm reading x Final volume (ml)}}{\text{Weight of sample (g)}}$$

3.5 DETERMINATION OF CESIUM IN LITHIUM, RUBIDIUM, CESIUM IN TUNGSTEN ORES, MINERALS AND BENEFICIATION PRODUCT AND MICA.

Scope

The method is standardized to analyse cesium in lithium, rubidium, cesium and tungsten ores, minerals and beneficiation products and mica by atomic absorption spectroscopy in emission mode.

Principle

The cesium is brought in solution by acid attack. The potassium dihydrogen orthophosphate and ammonium chloride has been used as ionization buffer to stabilize emission signal and severe background problems due to the formation of cesium molecular species in flame and the position of the cesium emission line in near infra-red region.

Reagents and Standards

1. **Hydrofluoric acid AR, 40%**
2. **Hydrochloric acid AR**
3. **Perchloric acid, AR**
4. **Nitric acid AR**
5. **Oxalic acid, 1% solution –** Dissolve 1 g. of AR oxalic acid in 100 ml distilled water
6. **Ammonium chloride -** Dissolve 50 g of ammonium chloride in 100 ml distilled water.
7. **Potassium dihydrogen orthophosphate K-40 mg/ml**. Dissolve 13.95 g AR potassium dihydrogen orthophosphate in 100 ml distilled water**.**
8. **(B) Standard cesium solution –**

Daily prepare fresh 1 ppm, 2 ppm and 5 ppm cesium standard for calibration of atomic absorption spectrometer scale.

Cesium Standard solution	Concentration ppm	Procedure
A	1000	Dissolve 0.1267 g cesium chloride in 100 ml. Distilled water
B	100	Dilute 10 ml. of (A) to 100 ml. with distilled water
C	10	Daily dilute 10 ml of (B) to 100 ml. with water
D	5	Take 50 ml. of (C) in a 100 ml. volumetric flask. Add 2 ml. Potash buffer and 2 ml. Ammonium chloride. Mix Add 2 ml. Conc. HCl and make volume to the mark with distilled water.
E	2	Take 20 ml. of (C) in a 100 ml. volumetric flask. Add 2 ml. Conc. HCl, 2 ml. Potash buffer and 2 ml. Ammonium chloride and make volume to the mark by distilled water.
F	1	Take 10 ml. of (C**)** 2 ml. of conc. HCl, 2 ml. Potash buffer, and 2 ml. Ammonium chloride in a 100 ml. Volumetric flask and make volume to the mark with distilled water.

Procedure

- Weigh appropriate quantity of sample (0.1 to 1.0 g). Transfer to a clean 100 ml. Capacity Teflon beaker. Record the weight to the nearest 0.0001 gm.
- Moisten with distilled water. Add 5 ml. nitric acid, 2 ml perchloric acid, and 5 ml hydrofluoric acid (40%) in that order.
- Carefully evaporate on a hot plate to dryness (Temp. 125-150^{o}C). Allow to cool to room temperature.
- Rinse inner walls of beaker with a little distilled water; add 2 ml. Conc. hydrochloric acid, 10 ml oxalic acid solution and 5 ml. Hydro fluoric acid. Mix by Teflon rod.
- Digest on a hot plate and then finally evaporate to dryness.
- Cool to room temperature, add 2 ml. Conc. hydrochloric acid, 2 ml potassium buffer, 2 ml ammonium chloride buffer and 25 ml distilled water and digest on a hot plate for 15 minutes.
- Filter the solution through Whatman filter paper No.40 into the 100 ml. volumetric flask.
- Wash the filter paper, cool to room temperature and dilute to volume.
- Calibrate the atomic absorption spectro-photometer as operational parameters of instrument given below :

Wavelength	852.1 nm
Slit width	0.2 nm
Instrument mode	Emission mode
Calibration parameter	1 ppm, 2 ppm, 5 ppm
Flame	Air, Acetylene

1. Atomise the standard solutions to calibrate concentration of cesium of unknown solutions.
2. When reading is not in calibration scale dilute original solution of sample to 10/20/50 fold volume

Calculation

$$\text{Cs ppm} = \frac{\text{Cs ppm reading x final volume (ml)}}{\text{Sample weight (g)}}$$

3.6 DECOMPOSITION AND ANALYSIS OF CHROMIUM IN ORE, MINERAL AND BENEFICIATED PRODUCTS FOR CHROMIUM, IRON, NICKEL AND COBALT.

Scope

Chromite mineral in general are not very easy to decompose and often present serious problems in obtaining reliable analytical results. The following procedure is rapid, accurate and precise for decomposition of chromite and estimation of chromium, iron, nickel and cobalt.

Principle

The chromite ore is decomposed by perchloric acid and hydrogen peroxide under reflux. The final measurement is performed by flame atomic absorption spectroscopy for determination of chromium, iron, nickel and cobalt.

Reagents and standards

1 **Perchloric acid AR,**
2 **Hydrogen peroxide 30% V/V AR**
3 **Round bottom flask corning 200 ml.**
4 **Reflux condenser, 45-60 cm. Length**
5 **Glass bubbler**
6 **Perchloric acid, 1%**
7. **Standard Chromium Solution**

Standard solution	Concentration ppm	Procedure
A	1000	Dissolve 2.829 potassium dichromate in 100 ml. water
B	100	Dilute 10 ml. of (A) to 100 ml by water
C	10	Dilute 10 ml of (B) to 100 ml. by water containing 2 ml. of perchloric acid and 88 ml water
D	5	Dilute 50 ml. of (C) in a 100 ml. by water containing 1 ml perchloric acid and 49 ml. Water.
E	1	Dilute 10 ml. of (C) in a 100 ml. by water containing 1.9 ml. Perchloric acid and rest water.

8. **Standard Iron Solution**

Standard solution	Concentration ppm	Procedure
A	1000	Dissolve 7.025 gm. ferrous ammonium sulphate in 1 litre. Water containing 20 ml. Perchloric acid
B	100	Dilute 10 ml. Of (A) to 100 ml by distilled water maintaining acidity 2% as perchloric acid
C	30	Dilute 30 ml of (B) to 100 ml. by maintaining acidity 2% perchloric acid
D	20	Dilute 20 ml. of (B) in a 100 ml. by maintaining acidity 2% perchloric acid
E	10	Dilute 10 ml. of (B) to 100 ml. having 2% perchloric acid.

9. Standard Nickel Solution

Standard solution	Concentration ppm	Procedure
A	1000	Dissolve 1.000 gm. Nickel material or nickel nitrate – 2.48 g in 10 ml. Conc. nitric acid and dilute to 1 litre.
B	100	Dilute 10 ml. of (A) to 100 ml keeping acidity 1% as HNO_3.
C	10	Dilute 10 ml of (B) to 100 ml maintain acidity 1% as HNO_3
D	5	Dilute 50 ml. of (C) in a 100 ml. By maintaining acidity 1% as HNO_3
E	3	Dilute 30 ml. of (C) to 100 ml. Keeping nitric acid 1% (V/V).
F	1	Dilute 10 ml of (C) to 100 ml by 1% nitric acid (V/V)

10. Standard Cobalt Solution

Standard solution	Concentration ppm	Procedure
A	1000	Dissolve 1 gm cobalt metal or 1.97 g. of cobalt chloride (CO $Cl_2.6H_2O$) in 10 ml. Conc. nitric acid and dilute to 1 litre.
B	100	Dilute 10 ml. of (A) by adding 1 ml nitric acid and 89 ml. Water.
C	10	Dilute 10 ml of (B) to 100 ml keeping 1% nitric acid
D	5	Dilute 50 ml. of (C) in a 100 ml. By maintaining acidity 1% as HNO_3
E	3	Dilute 30 ml. of (C) to 100 ml. Keeping nitric acid 1% (V/V).
F	1	Dilute 10 ml of (C) to 100 ml by maintaining acidity 1%, as HNO_3

Procedure

- Transfer about 0.1000 g. finely powder (200 mesh) chromite sample to a borosil round bottom flask.
- Fit a vertical condenser (Water) to the flask. Cautiously add 10 ml. Perchloric acid and 5 ml hydrogen peroxide.
- Second end of the condenser is connected to a glass bubbler immersed in a deep receptacle (50 ml. Measuring cylinder containing 20 ml of 1% perchloric acid.
- The contents of round bottom flask are heated to copious fumes of perchloric acid for three hour.
- The flask is cooled to room temperature
- Add 5 ml of perchloric acid and 2 ml hydrogen peroxide
- Again reflux the contents of the flask to copious fumes for one hour
- The black particles of chromite are dissolved completely, and then cool to room temperature.
- The glass bubbler and condenser are rinsed with water. The abosorbing 1% perchloric acid in measuring cylinder is added to the flask.
- The solution is filtered through Whatman filter paper No.40 (pretreated with dilute perchloric acid solution) washed.
- Filtrate is cooled to room temperature and quantitatively transferred to a 100 ml. volumetric flask and make volume to the mark by distilled water. Mix thoroughly.
- Calibrate the atomic absorption spectrometer as per the manufacturer’s instruction for chromium, iron, nickel and cobalt. The operating parameters of instrument are as below

Parameters	**Cr**	**Fe**	**Ni**	**Co**
Wave length (nm)	357.9	372.0	232.0	240.7
Slit width (nm)	0.2	0.2	0.7	0.2
Lamp current (mA)	6	7	25	25
Instrument mode	Absorbance	Absorbance	Absorbance	Absorbance
Standards for Scale calibration (ppm)	1,5,10	10,20,30	1,3,5	1,3,5
Flame	Acetylene/N_2O	Acetylene/Air	Acetylene/Air	Acetylene/Air

1. Atomise the standards solutions and sample solution and record the reading in calibration scale range.
2. Dilute the sample solution as per requirement to D/10, D/50, D/100 fold volume by water keeping acidity 2% as perchloric acid.

Calculation

$$\begin{array}{l} \%\,\text{Cr or} \\ \%\,\text{Fe or} \\ \%\,\text{Ni or} \\ \%\,\text{Co} \end{array} = \frac{\text{Metal ppm reading x Total vlume (ml) x 100}}{10^6 \text{ x sample weight (g)}}$$

3.7 DETERMINATION OF SILVER BY ATOMIC ABSORPTION SPECTROSCOPY IN POLYMETALLIC ORES AND BENEFICIATED PRODUCTS

Scope

This method has been designed to determine silver in polymetallic ores and beneficiated products by atomic absorption spectroscopy.

Summary of method

A sample is treated with reverse aquaregia (3 HNO_3 : 1 HCl), which breaks down the sample converting the silver to soluble nitrate compound. The syrupy mass is treated with aqueous ammonia solution, the silver dissolves as silver ammonia complex and is separated from flocculent precipitate of iron, etc. The silver is analyzed by atomic absorption spectrophotometry calibrated by silver standards containing same quantity of reagent matching to unknown samples.

Reagents and standards

1. **Nitric acid Ar**
2. **Hydrochloric acid AR**
3. **Standard solution**

Standard solution	Concentration ppm	Procedure
A	1000	Dissolve 1.5748 g silver nitrate in water and dilute to 1 litre
B	100	Prepare fresh by diluting 10 ml of (A) to 100 ml with distilled water
C	10	Prepare fresh by diluting 10 ml of (B) to 100 ml with distilled water
D	3	Prepare fresh by diluting 30 ml of (C) to 100 ml by adding 15 ml NH_3 (1:1) and 55 ml distilled water
E	2	Prepare fresh by diluting 20 ml of (C) to 100 ml by adding 15 ml NH_3 (1:1) and 65 ml distilled water
F	1	Prepare fresh by diluting 10 ml of (C) to 100 ml by adding 15 ml NH_3 (1:1) and 75 ml distilled water

Procedure

- Transfer 2.0 gram sample into a 250 ml beaker and moisten the sample with water.
- Add 20 ml reverse aqua regia ($3HNO_3$: 1HCl).
- Carefully stir this mixture with the glass rod and place the beaker on the hot plate (maximum surface temperature 100-150^{o}C) and allow to evaporate to a syrupy mass.
- Remove the beaker from the hot plate, allow to cool to room temperature, add 15 ml of 1:1 ammonia solution and stir with glass rod.
- Quantitatively transfer the total content to a clean 100 ml volumetric flask, dilute to volume and mix thoroughly.
- Dry filter it into a 50 ml volumetric flask (using dry funnel and dry flask).
- Determine silver by reading absorbance by atomic absorption spectrometer calibrated by standards of silver containing matching quantity of reagents used for sample preparation.

- **Other instrumental parameters are as mentioned below :**

Wavelength	328.1 nm
Slit width	1.00 nm
Lamp current	15 mA
Instrument Mode	Absorbance BC
Calibration range	1 ppm – 3 ppm

Calculation

$$\text{Ag ppm} = \frac{\text{Ag ppm Reading x Volume (ml) x Dilution factor}}{\text{Weight of sample (g)}}$$

3.8 DETERMINATION OF MOLYBDENUM IN TUNGSTEN AND POLYMETALLIC ORES, MINERALS AND BENEFICIATION PRODUCTS.

Scope

The method is standardized for determination of molybdenum in tungsten and polymetallic ores, minerals and beneficiation products. The application can be extended to other types of minerals and ores by essential modification in decomposition pattern**.**

Principle

The method involves decomposition of finely powdered sample by aqua-regia. The acidity of the solution is maintained at 20% with respect to hydrochloric acid. The aluminium chloride or sodium sulphate is added as ionization corrector/modifier to stabilize absorption signal and baseline.

Reagents and standards

1. **Nitric acid, Ar**
2. **Hydrochloric acid, AR**
3. **Aluminium chloride solution (10%) –** Dissolve 10 gm of anhydrous aluminium chloride in 0.1 N 100 ml hydrochloric acid cool to room temperature.
4. **Sodium sulphate – (10%) –** Dissolve 10 gm of AR sodium sulphate in 100 ml distilled water.
5. **(A) Standard molybdenum solution – 1000 ppm –** Dissolve 2.0425 g ammonium molybdate ($(NH_4)_2 MoO_4$) in distilled water and dilute to one litre

   (B) Standard molybdenum solution – 100 ppm Dilute 10 ml of (A) to 100 ml by distilled water.

   (C) Standard molybdenum solution – 10 ppm – Dilute 10 ml of (B) to 100 ml by distilled water.

   (D)Standard molybdenum solution – 5 ppm – Daily prepare fresh by taking 50 ml of (C), 10 ml of aluminium chloride buffer, 20 ml conc. hydrochloric acid and 20 ml distilled water in 100 ml volumetric flask. Mix well.

   (E) **Standard molybdenum solution – 3 ppm** – Daily prepare fresh by taking 30 ml of (C), 10 ml of aluminium chloride buffer, 20 ml conc. hydrochloric acid and 40 ml distilled water in 100 ml volumetric flask. Mix well.

   (F) **Standard molybdenum solution – 1 ppm** – Take 10 ml of (C) in a 100 ml volumetric flask. Add 10 ml aluminium chloride buffer and 20 ml. Conc. hydrochloric acid. Mix. Make to the mark by distilled water. Daily prepare freshly.

Procedure

- Transfer 0.2000 to 0.5000 g finely powdered sample to a clean 250 ml beaker.
- Add 10 ml concentrate hydrochloric acid; mix the content by glass rod. Cover by a watch glass.
- Digest on a hot plate (temperature range 125-150^{o}C) for about half an hour cool.
- Carefully add 20 ml aquaregia by measuring cylinder. Cover and digest on hot plate for two hours.
- Remove watch glass and slowly evaporate the acid to a syrupy residue.
- Cool. Add 20 ml concentrate hydrochloric acid and 25 ml water. Heat just to boil. Filter in a 100 ml volumetric flask wash beaker and residue with 1% hot hydrochloric acid. Cool the filtrate. Add 10 ml aluminium chloride buffer. Make volume to mark by distilled water. Mix well.
- Read absorbance of molybdenum by atomic absorption spectrophotometer calibrated by molybdenum standards.
- The instrument parameters for operation are as under :

Wavelength	313.3 nm
Slit width	0.2 nm
Lamp current	7.0 mA
Instrument mode	Absorbance BC ON
Calibration parameter	1 ppm, 3 ppm, 5 ppm
Flame	N_2O Acetylene

Calculation

$$\text{Mo ppm} = \frac{\text{Mo ppm reading x volume (ml) x Dilution factor}}{\text{Wt. of sample (g)}}$$

3.9 DETERMINATION OF BISMUTH IN TUNGSTEN AND POLYMETALLIC – ORE, MINERALS AND BENEFICIATION PRODUCTS BY ATOMIC ABSORPTION TECHNIQUE.

Scope

This procedure is used for the quantitative measurement of bismuth, which is present in tungsten and polymetallic – ores, minerals and beneficiation products.

The sample is treated with aqua regia (3HCl : 1 HNO_3), which breaks down the mineral converting the elements to soluble chloride compounds. The syrupy mass is dissolved in hydrochloric acid, and the potassium chloride is added as ionization buffer/conditioner to stabilize absorption signal.

Reagents & Standards

1. **Nitric acid AR**
2. **Hydrochloric acid AR**
3. **Potassium chloride (ionization buffer)** – Dissolve 16.3 gm AR potassium in 100 ml distilled water.
4. **Standard solution of Bismuth :**
   - A. **Bismuth standard – 1000 ppm** : Dissolve 1.000 g bismuth metal (99.999%) in 8 ml of 10 M nitric acid, boil gently to expel brown fumes of nitrates, and dilute to 1 litre volume by distilled water and 250 ml hydrochloric acid.
   - B. **Standard Bismuth solution – 100 ppm** : Dilute 10 ml of standard (A) to 100 ml by adding 24 ml concentrated hydrochloric acid and 66 ml water.
   - C. **Standard Bismuth solution – 10 ppm** : Dilute 10 ml of standard (B) to 100 ml by adding 24 ml concentrated hydrochloric acid and 66 ml water.
   - D. **Standard Bismuth solution – 5 ppm :** Dilute to 50 ml of standard (C) to 100 ml by adding 12.5 ml concentrate hydrochloric acid and 37.5 ml of water.
   - E. **Standard Bismuth solution – 1 ppm :** Dilute 10 ml of standard (C) to 100 ml by adding 24 ml of concentrate hydrochloric acid and 66 ml of water.

Procedure

- Transfer 0.1000 to 0.5000 g of finely powdered sample to a 250 ml beaker. Moisten the sample with water.
- Add 100 ml concentrate hydrochloric acid, carefully stir this mixture with glass rod and place the beaker on the hot plate (max. temperature 125-150^{o}C) and digest for 30 minutes.
- Using a graduated cylinder, carefully add 10 ml of aqua-regia, mix and evaporate on hot plate to a syrupy mass.
- Cool and add 25 ml hydrochloric acid. Heat to boil and add some distilled water.
- Filter it in a 100 ml volumetric flask quantitatively; wash the residue thoroughly with hot 5% hydrochloric acid.
- Add 10 ml potassium chloride ionization buffer and make volume to 100 ml by water. Mix well.
- Read absorbance of bismuth by atomic absorption spectrometer
- The instrumental parameters are as under :

Wavelength	223.1 nm
Slit width	0.2 nm
Lamp current	12 mA
Instrument mode	Absorbance BG ON
Calibration range	1 ppm, 5 ppm, 10 ppm
Flame	Air – Acetylene

Calculation

$$\text{Bi ppm} = \frac{\text{Bi ppm reading x volume (ml) x Dilution factor}}{\text{Weight of sample (g)}}$$

3.10 DETERMINATION OF OXIDIZED ZINC IN A ZINC ORE, ZINC CONCENTRATE AND BENEFICIATED FRACTION.

Scope

The method is standardized for estimation of oxidized zinc in zinc ore, its concentrate and beneficiated fraction by atomic absorption spectroscopy.

Principle

An appropriate weight of the representative sample is digested with ammonium chloride and ammonium acetate. The zinc is analyzed by atomic absorption spectroscopy. An identical reagent blank is run for correction of reagent absorbance.

Reagents and Standards

1. **Ammonium chloride** – Dissolve 25 gm AR ammonium chloride in 100 ml distilled water.
2. **Ammonium acetate** – Saturated solution in distilled water.
3. **Stock standard for Zinc**
   - (A) **1 ml of solution = 1 mg of zinc (1000 ppm) –** Dissolve 1.0000 gm zinc metal in 10 ml of hydrochloric acid, dilute to 1 litre by distilled water.
   - (B) **Zinc standard stock solution – 100 ppm:** Dilute 10 ml of A to 100 ml with 1% (V/V) nitric acid.
   - (C) **Zinc standard stock solution – 10 ppm:** Daily dilute 10 ml of B to 100 ml with 1% nitric acid (V/V).
   - (D) **Zinc Standard – 1 ppm:** Daily dilute 10 ml of C to 100 ml with 1% nitric acid (V/V).
   - (E) **Zinc Standard Solution – 0.5 ppm**: Prepare daily by diluting 50 ml of D to 100 ml with 1% nitric acid (V/V).

Procedure

- To 1.000 gm of sample in a 250 ml beaker, add 20 ml of ammonium chloride solution and 10 ml of ammonium acetate solution by pipette. Add 25 ml of distilled water.
- Cover, digest on hot place for 10 minutes, filter by Whatman filter paper No.40 and wash with hot water containing ammonium chloride (0.2 gm/litre).
- Add 2 ml nitric acid just boil.

- Cool to room temperature and transfer to a 100 ml volumetric flask.Add distilled water to mark.
- Run an identical reagent blank for absorbance correction.
- Read the absorbance on atomic absorption spectrometer. The operating conditions of instruments are as under.

Wavelength	213.9 nm
Slit width	0.7 nm
Lamp current	5.0 mA
Calibration range	0.5 ppm – 1.5 ppm

Calculation

$$\% \text{ Zn} = \frac{\text{Zn ppm reading x volume (ml) x Dilution x 100 factor}}{10^6 \text{ x sample weight (gm)}}$$

3.11 DETERMINATION OF OXIDIZED LEAD IN LEAD ORE, LEAD CONCENTRATE AND OTHER BENEFICIATION FRACTIONS.

Scope

The method has been standardized for the determination of oxidized lead in its ore, concentrate and beneficiation fractions. In this method all but the sulfide and chromate of lead are soluble.

Principle

An appropriate weight of the finely ground sample is digested with saturated ammonium acetate solution. The extracted lead salts are estimated by an atomic absorption spectrophotometer running an identical reagent blank.

Reagents and Standards

1. **Ammonium acetate saturated water solution.**
2. **Nitric acid AR**
3. **(A) Stock standard solution of Lead – 1000 ppm :** Dissolve 1 gm lead metal (99.999%) in 10 ml nitric acid and dilute to 1 litre.
   (B)Lead standard solution – 100 ppm : Dilute 10 ml of (A) to 100 ml with 1% nitric acid (V/V).
   (C) Lead standard solution – 10 ppm : Prepare daily by diluting 10 ml of B to 100 ml with 1% nitric acid (V/V).
   (D) Lead standard solution – 5 ppm : Prepare daily by diluting 50 ml of (C) to 100 ml with 1% nitric acid.
   (E)Lead standard solution – 1 ppm : Prepare daily by diluting 20 ml of (D) to 100 ml with 1% nitric acid.

Procedure

- To 1 gm of the 100 mesh –150 mesh sample in a 250 ml beaker, add 10 ml of saturated solution of ammonium acetate and 50 ml of water.
- Digest on a steam bath for 1 hour and then boil for a while.
- Cool and filter through Whatman filter paper No.40, wash with hot water.
- Add 2 ml nitric acid, boil.
- Cool and transfer to a 100 ml volumetric flask. Make volume to mark. Run a reagent blank.
- Measure absorbance on atomic absorption spectrometer calibrated to 1.0, 5.0 and 10 ppm.
- Other operation parameters of instruments are as below :

Wavelength	217 nm
Slit width	1.0 nm
Lamp current	4.0 mA
Instrument mode	Absorbance BG ON

Calculation

$$\% \text{ Pb} = \frac{\text{Pb in ppm reading x volume (ml) x Dilution factor x 10}}{10^6 \text{ x Weight of sample (gm)}}$$

3.12 DETERMINATION OF OXIDIZED COPPER IN COPPER ORE/CONCENTRATES.

Scope

This method has been standardized for the determination of oxidized copper in copper ore/concentrates and beneficiated fraction by atomic absorption spectroscopy.

Principle

This method provides a separation of the copper in oxidized form as in cuprite, tenorite, malachite, and chrysocolla from that in the sulphide form as in chalcocite, covellite and chalcopyrite. An appropriate weight of the representative sample is digested with sulphurous acid. The digested copper is analysed in filtrate by atomic absorption spectroscopy.

Reagents and Standards

1. **Sulphurous acid (H_2SO_3) – 3%**
2. **Stock standards for copper –** 1 ml of solution = 1 mg of copper (1000 ppm).

Procedure

- Weigh exactly to 2.5 g of the representative sample, ground to fineness of 100 to 150 mesh in a bottle and add 50 ml of 3 per cent solution of sulphurous acid. Cork the bottle tightly and agitate by wrist type shaker for 15 minutes.
- Then transfer the content of the bottle to a beaker, cover with watch glass, and digest on steam bath for 5-10 minutes.
- Filter by Whatman filter paper No.40, wash the residue with sulphurous acid solution for at least for to five times, add the washings to the filtrate, which will contain in solution all oxides, carbonates and silicates of copper, and all metallic copper.
- Boil the filtrate to remove sulphurous acid. Then add 2 ml nitric acid and just boil, cool and make 100 ml in a volumetric flask.
- Read the absorbance on atomic absorption spectrophotometer GBC-932 model calibrated in working range 1 ppm to 5 ppm.

- **Operating condition for instrument are :**

Wavelength	324.7 nm
Slit width	0.5 nm
Lamp current	4.0 mA
Instrument mode	Absorbance BG On
Flame	Air-Acetylene – Blue flame

Calculation

$$\% \text{ Cu} = \frac{\text{Cu ppm reading x volume (ml) x 100 x Dilution factor}}{10^6 \text{ x weight of sample (gm)}}$$

3.13 DETERMINATION OF NIOBIUM AND TANTALUM IN ORES AND ORE DRESSING PRODUCTS OF TUNGSTEN AND TIN.

Principle

The niobium and tantalum are co-precipitated with titanium in presence of 10% zinc-ethylene tetramine acetate complex to isolate and separate from tungsten, tin, zirconium, chromium, molybdenum and iron. The estimation is finished by AAS in presence of iron as ionization/stabilization buffer in fluoride media.

Reagents and standards

1. **Niobium standard 1000 ppm** – Transfer 1.000 g niobium metal (or 1.4305 g Nb_2O_5) to a platinum dish, add 20 ml hydrofluoric acid, and heat gently to complete dissolution, dilute to 1 litre. Prepare 100 ppm niobium standard by proper dilution maintaining 2 ml HF/100 ml. volume (Use Teflon ware).

2. **Tantalum standard – 1000 ppm** - Take 1.000 g tantalum metal (or 1.2210 g Ta_2O_5) in platinum dish (or Teflon dish), add 20 ml HF, gently heat to dissolve. Dilute it to 1 litre with water. To prepare 100 ppm tantalum standard, dilute 10 ml of 1000 ppm stock standard to 100 ml keeping 2 ml. HF/100 ml volume.
3. **Zinc solution (1 M) –** Dissolve 21.937 g of zinc acetic acid and dilute to 100 ml.
4. **Ethylene diamine tetracetate sodium salt solution (1 M)** : Dissolve 37.31 g of AR EDTA sodium salt in warm water and dilute to 100 ml.
5. **Zinc-EDTA Complex (1:1) (10%)** – Mix 10 ml zinc solution with 10 ml EDTA solution and dilute to 100 ml with water.
6. **Ammonia solution -** 1:1
7. **Instrumental parameters :**

An atomic absorption spectrometer equipped with nitrous oxide – acetylene burner. The instrumental operating parameters are as under**:**

Parameters	**Niobium**	**Tantalum**
Wavelength	334.9 nm	271.5 nm
Slit width	0.2 nm	0.2 nm
Lamp current	20 mA	20 mA
Flame	Nitroous oxide Acetylene	Nitrous oxide Acetylene

The flame should be adjusted to a slight yellowness where absorption of niobium and tantalum is optimum.

Procedure

- **Decomposition of sample**: Fuse a sample weighing 0.5000 to 1.0000 with 5 g sodium hydroxide in an iron crucible at 550°C in muffle furnace. Cool the crucible, leach the melt with water, and boil for few minutes. Filter the precipitate using Whatman filter paper No.40 and wash with 1% sodium hydroxide solution. The chromium, tungsten, tin, molybdenum, silicon and aluminium pass in the filtrate, and the precipitate contains iron, titanium, niobium and tantalum. Transfer precipitate into a 400 ml beaker. Wash filter several times with 5% sulphuric acid containing a few drops of hydrogen peroxide. Heat to boil to dissolve precipitate.
- **Separation :** Add 5 ml 1:1 sulphuric acid ot the solution and boil it to destroy hydrogen peroxide. Add 20 ml of titanium solution (1 mg TiO_2/ml) and 10 ml of zinc EDTA solution. Heat the solution just to boil and neutralize with dilute ammonia solution adding a few drops in excess. Just boil the precipitate of Ti, Nb and Ta, separate the precipitate on Whatman filter paper No.41. Wash the precipitate with very dilute hot ammonia solution. Transfer the precipitate to a platinum dish by a small quantity of water. Carefully wash the filter paper with 5 ml. of hydrofluoric acid to dissolve and bring any niobium

and tantalum adhered to filter paper. Add 1 ml 1:1 sulphuric acid and heat to dissolve precipitate. Cool the solution, add 2.5 ml iron solution (50 mg/ml prepared in 10% HF (V/V) and dilute to 25 ml in a Teflon volumetric flask. Mix.

- **Measurement:** Set atomic absorption spectrophotometer to the instrument operation parameters mentioned above. Calibrate instrument scale by 1, 3 and 5 ppm. Matching standard solution of niobium and tantalum containing 2.5 ml iron solution and 2.5 ml titanium solution (20 mg/ml) in 25 total volume. The clear sample solution is aspirated into the flame to measure atomic absorption and metal concentration in ppm**.**

Calculation

$$\text{ppm Nb or Ta} = \frac{\text{ppm Nb/Ta reading x volume (ml)}}{\text{Sample weight (g)}}$$

3.14 DETERMINATION OF GALIUM, INDIUM, THALLIUM IN ZINC AND LEAD ORE AND BENEFICIATION PRODUCT BY ATOMIC EMISSION ON ATOMIC ABSORPTION SPECTROPHOTOMETER.

Scope

The method is optimized for estimation of gallium, indium and thallium in ores and ore dressing products of lead and zinc by atomic emission technique involving separation and pre-concentration by tributyl phosphate. The method is also applicable to bauxite, aluminium metal and its alloys.

Principle

The sample is brought in solution by acid treatment the gallium indium and thallium are separated and preconcentrated by solvent extraction in tributyl phosphate containing sodium nitrite. The emission is measured by atomic absorption spectrometer.

Reagents and standards

1. **Tributyl phosphate, AR**
2. **Hydrochloric acid, AR 6 M**
3. **Nitric acid 1 M**
4. **Sodium nitrite, crystalline**
5. **Gallium, indium and thallium standard –** Prepare gallium, indium and thallium standard 100 mg/ml and by serial dilution 1 mg metal/ml.
6. **Ionisation buffer 2 mg Cs/ml.** Dissolve 0.2543 g CsC1 in 100 ml water**.**
7. **Ionisation buffer 5 mg Na/ml**. Dissolve 1.275 g NaCl in 100 ml water.

Instrumental parameters: The emission intensity is measured on atomic absorption spectro photometer in emission mode.

Instrumental parameters	**Gallium**	**Indium**	**Thallium**
Wavelength, nm	403.3	451.1	535.1
Slit width, nm	0.20	0.20	0.50
Instrument Mode	Emisstion	Emission	Emission
Calibration Standards mg/ml	1, 3, 5	1, 3, 5	1, 3, 5
Flame	AC:N_2O	AC:N_2O	AC:N_2O

AC = Acetylene

Procedure

Decomposition of sample :

- Sulphides of lead and zinc **:** Roast 2.000 g sample (-150 mesh) in a porcelain dish at 600°C for 3 hours in a muffle furnace Transfer roasted sample to a 250 ml beaker, add 25 ml aquaregia. Keep beaker initially at room temperature for one hour and then slowly heat at low temperature on a hot plate. Finally evaporate the acid, bring residue in solution by 25 ml 6N hydrochloric acid. Boil, filter, wash residue with 6 N hydrochloric acid. Use this solutin for further steps**.**
- **Aluminium metal**: Treat clean 2.000 g aluminium metal with 6 M hydrochloric acid. Boil to dissolve it and make it to 50 ml. Use an appropriate aliquot for further steps.
- **Bauxite**: Fuse sample weighting 0.5000 to 1.0000 g with 2 gm of sodium hydroxide and 0.5 g Na_2O_2 in an iron/zinconium crucible at ~ 550°C. Leach the cake with hot water. Dissolve precipitate in hydrochloric acid. Maintain acidity by conc. hydrochloric acid**.**

Separation, preconcentration and measurement:

- **Preconditioning of tributyl phosphate:** Take 150 ml tributyl phosphate in a 500 ml separating funnel. Add 50 ml 5% sodium carbonate solution. Shake well for two minutes. Let separate layers, discard lower aqueous layer. Now add 50 ml 6M hydrochloric acid shake it for 2 minutes and discard acid layer.
- **Pre-concentration:** Transfer the sample to a 125 ml. separatory funnel; add hydrochloric acid to keep 3M hydrochloric acid concentration for extraction. Now add 25 ml of tributyl phosphate and a few crystals of sodium nitrite shake the solution for 2 minutes. Let two phases separate transfer aqueous phase to another separating funnel extract it two times more with 10 ml portion of fresh tributyl phosphate. Mix all the three extracted portions of organic phases and transfer to 125 ml separatory funnel. Wash the tributyl phosphate twice with 10 ml portions of 6M hydrochloric acid by shaking.

Now strip down gallum, thallium and indium from tributyl phosphate extract by shaking with 10-15 ml 1% hydrochloric acid (V/V) for two minutes. Collect the aqueous phase in 100 ml beaker. Repeat extraction with 10 ml 1% hydrochloric acid containing 0.1 g of sodium sulphite. Combine all the three aquous extracts and evaporate on a steam bath to about 5 ml. Cool and transfer to a 25 ml volumetric flask, add 5 ml cesium or sodium ionization buffer solution and make it to volume mix.

Measurement

Aspirate the solution into the nitrousoxide – acetylene flame – red zone and measure the emission intensity and ppm reading of gallium, indium and thallium.

Calculation

$$\text{ppm Ga or In or Tl} = \frac{\text{Metal ppm reading x volume (ml)}}{\text{Sample weight (g)}}$$

Note:

1. A little sodium nitrite should be added to the solution to oxidize thallium (I) to thallium (III), which is readily extracted into tributyl phosphate at 3.6 M hydrochloric acid concentration.
2. The thallium is readily stripped into aquous phase under reducing conditions and so a few crystals of sodium sulphite should be added.

4. Principle And Procedure of Carbon and Sulphur Analyser

Principle

A sample held in a ceramic crucible is pyrolysed in the RF furnace. The combustion atmosphere is technical grade oxygen, which flows through a guide tube to the sample after being free from water vapour and carbon dioxide in a filtration system. The C and S contained in the sample are oxidized to carbon dioxide and sulphur dioxide respectively in the pyrolysis. The oxygen flow serves both as oxidizing agent and as system carrier gas.

The entrained gaseous combustion products leaving the furnace are passed through dust and water vapour filters and through a thermostatic pressure regulator and flow rate regulator system and into the analysis cells of IR analyzer which provides output signals which are proportional to the respective concentration of CO_2 and SO_2 in the carrier gas flow and finally the concentration of C and S contained in each sample will be shown in percent by weight on Visual Display UnitVDU.

Procedure

Switch on the instrument and connect the compressed air supply at the instrument rear panel by using polyamide tubing provided, open the compressed air supply. The required overall pressure is 4 to 6 bar. Open the oxygen cylinder and O_2 pressure of (6 to 10 bar) is to be adjusted by means of external pressure regulator. Let the instrument on in "Stand by mode" for 30 minutes to warm up.

Fire the crucibles (sample holders) for approximate 45 minutes at $950^{o}C$ in the furnace before analysis then keep it in a desiccators for cooling. Weigh around 1 part Iron accelerator and 3 parts tungsten accelerator and afterwards take 0.15 g to 0.2g of standard in the crucible and enter the weights from balance to VDU then select "Calibration Mode." Select the standard range which one is suitable for the sample and calibrate the instrument. After this the same procedure is to be followed for the sample and sample is pyrolysed in the RF furnace and C&S contained in the sample are oxidized to CO_2 & SO_2 respectively by means of oxygen and fed to the analysis cells of IR analyzer where the intensity is measured and converted into C&S concentration in percent by weight and finally display on VDU.

Application

- In steel and cast samples for complete combustion tungsten accelerator as additive material is required.
- In non-metallic samples, high purity iron plus tungsten as additive is to be added.
- Samples in the form of shavings or chips yield optimal conditions for the measurement, since their relatively large surface areas promote oxidation.

- For sample in the form of dust or fine powders, there exists the possibility that the O_2 flow from the guide tube will blow samples particles from the crucible, thus falsifying the sample weight. The result will be measured concentrations, which are too low or non-reproducible. Thus the sample surface be well covered by the diluent material.

Precautions

- It is necessary to add to the sample a metallic additive material in order to guarantee a complete combustion of the sample material and for complete oxidation.
- The additive material should be free from the element to be analysed.
- It must not form stable chemical compounds with the element of the sample to be analysed.
- Combustion tube and dust traps should be cleaned after every 30-50 analysis.
- For reproducibility of the results one should take precaution that sample as well as diluent material or accelerator should not be contaminated and it should be homogeneous.
- Check the leakage in the gas flow, combustion tube should be clean and the carrier gas should be moisture free.

5. Method of Analysis Using Inductively Coupled Plasma ICP) Instrument

5.1 ICP (AES) – TECHNIQUES AND APPLIICATIONS

ABSTRACT

Plasma Spectrometry is one of the most popular and versatile techniques of geological and environmental samples, including rocks and minerals, waters, dust, vegetation, soils and sediments. Inductively coupled plasma is used as emission source in ICP-atomic emission spectrometry (ICP-AES) and due to wide dynamic range of ICP, it can measure elements over an extremely wide range of concentrations. Plasma spectrometry is primarily a solution-based techniques and the dissolution step controls both the range of elements quantifiable and the limits of determination considering the detection limit and spectral interferences. However, chemical separation and preconcentration steps are required for the Rare Earth Elements, precious metals and several other elements, which enable determination to be made at ppb levels. ICP-AES is best used for major, minor and trace elements determinations.

INTRODUCTION

ICP-AES instruments are based on the principle that by viewing the appropriate region in an Ar-Plasma tail flame, the atomic and ionic emission lines of analytes can be measured against very low background emission intensities. The very high temperature (up to 10,000^oK) in the ICP ensures for more efficient atomization and consequently the chemical interferences are very less. ICP-AES exhibits very wide linear response range of more than 5 order of magnitude, making it possible to determine major, minor, and trace and ultra-trace elements in a single preparation.

Plasma Formation

A water-cooled gold or silver plated copper tube is coiled around the upper part of the plasma torch. The coil is connected to a RF-Generator, which creates an oscillating RF magnetic field within the Ar flowing through the torch. RF-Generators operate within the industrial frequency bands of 27.12 MHz or 40.68 MHz and most systems are operated at forward powers of 0.9 to 1.5 KW.

The Ar stream passing through the torch is initially seeded with electrons, generally using a high-voltage spark. The electrons are subjected to intense oscillations of the RF magnetic fields generated by the induction coil and collide with Ar atoms causing ionization. Each charged particle formed in the gas stream is controlled by the magnetic fields, which force it to flow in a closed annular path within the torch. Resistance to the induced motion of the charged particles causes ohmic heating of the gas stream, which rapidly rises in temperature to approximately 10,000^oK. This transfer of energy by inductive coupling to form high temperature plasma is the definitive characteristic of an ICP.

SAMPLE PREPARATION METHODS

1. Water and Biological Samples

Plasma spectrometry is primarily a solution technique. Dissolved samples like natural waters, biological fluids, beverages, oils, etc. require minimum sample preparation. For waters, acidification with HNO_3 and then filtration or centrifuging to remove particulate matter is normally required. Biological fluids and beverages require dilution but are then ready for direct analysis. Botanical samples must first be ashed to ensure their complete decomposition. This will involve wet or dry ashing of the samples**.**

2. Geological Samples

Geological samples dissolution procedures are divided into three broad groups

- Leaching of the sample with mineral acids e.g. HCl-HNO_3-$HClO_4$ etc.
- HF-$HClO_4$ acid attack of the sample
- Fusion methods

i. Acid Leaching

For many elements in geological samples, the complete dissolution of the sample is not necessary. In many cases, a simple leaching of the elements of interest by some combination of mineral acids (HCl-HNO_3-$HClO_4$) is quite adequate. Some elements such as As and Sb will be lost if HCl is used without HNO_3.

ii. HF-$HClO_4$ Dissolution

The samples are attacked with HNO_3-HF-$HClO_4$ mixture in Teflon beakers on hot plate, which are then evaporated to dryness, followed by final dissolution of samples in dilution HNO_3. But the Si, Se & B will be lost**.**

iii. Fusion Method

Of these methods, the fusion methods are considered the most rigorous and complete. The type of flux used will be dependant on the analytical requirement, the nature of the samples and the range of elements to be determined. The most popular flux is lithium meta-borate ($LiBO_2$), sodium carbonate, potassium carbonate, sodium hydroxide, sodium peroxide, potassium hydroxide and potassium-bi-fluorite (KHF_2).

The major disadvantage of all fusion procedures is that they introduce large quantities of total dissolved solids (TDS), which necessitate increased dilution. These increased dilutions will push some trace element concentrations below the limit of quantitative analysis. The fusion procedures may also lead to increased loss of volatile elements.

SEPARATION AND PRECONCENTRATION PROCEDURES

Despite low instrumental detection limits, spectral interferences and /or other matrix effects preclude the determination of several trace elements in samples. These difficulties may be overcome by using chemical procedures, which separate groups of analyte from their matrix. Elemental groups, which are routinely analysed in this way include the –

1. Hydride forming elements e.g. As, Bi, Ge, Pb, Sb, Se, Sn, Te & Hg.
2. REE's e.g. La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb & Lu.
3. Platinum Group Elements – Ir, Os, Pd, Pt, Rh & Ru.

1. HYDRIDE ELEMENTS

A number of elements will readily form gaseous hydrides at ambient temperatures. Many of these hydride elements are toxic in the environment and are important mineral exploration targets or pathfinders. However, they occur at very low concentrations in samples and are subject to major spectral interferences from other matrix elements and their determination requires separation procedure.

Hydride formation is achieved by reacting samples with aqueous $NaBH_4$, as the reducing agent and the element in hydride form directly goes to the Plasma and the interference elements remains in the solution. Therefore, hydride generation allows 100% efficient injection of these elements into dry Plasma without the use of nebulisation. Thus very low concentration of these elements can easily be determined by this method due to the high efficiency of analyte transfer via. hydride generation and the removal of interference caused by matrix elements.

Recommended wavelengths and typical detection limits

Element	Wavelength	Detection limit in mg/L (ppm)
As	189.04	0.5
Se	196.09	0.5
Hg	184.95	0.1
Sn	189.98	0.2
Te	214.30	1.0
Bi	223.06	0.7
Sb	206.83	0.5
Ge	303.91	0.06

2. RARE EARTH ELEMENTS

The lanthanum group elements from atomic number 57 to 71 are found in nature in stable form and the analysis of rare earth elements is very important in ores and other geological samples. For the determination of the rare earth elements, it is essential that all the minerals that contain the rare earths have been fully dissolved. The mineral zircon contains large number of REE, with a concentration of the heavier rare earths and it is not quantitatively dissolved in the standard HF/$HClO_4$ attack. It is essential that the sample must be completely dissolved, either using an acid attack followed by a mini fusion of the insoluble residue with NaOH, $LiBO_2$ or $K_2S_2O_7$ or fusion of the complete sample.

Procedure

(1) Weigh 0.5 gm sample in a Teflon beaker and add 5 ml $HClO_4$ and 12 ml. HF in it. After stirring, the solution is evaporated on hot plate to dryness, cooled and dissolved in 20 ml. 3 N HCl. The solution is filtered and the residue is ignited at 800°C in a silica crucible. Transfer the residue in nickel crucible and fuse it with NaOH on burner. After cooling, the flux is dissolved in 25 ml (25% HCl) and the solution is added to the filtrate. The whole solution is evaporated on the hot plate till dry. Then add 10 ml. 2N-HCl solution and heat it on hot plate for about 20 minutes to dissolve the residue. This solution is poured in the column charged with Biograd AG50W-X8 H-form, 200 to 400 mesh, conditioned in 2N-HCl.

(2) Weigh 3.0 gm. sample in Teflon beaker and add 30 ml conc. HCl and 10 ml concentration HNO_3 in it. Keep the beaker on hot plate and digest it for 30 minutes. Add 10 ml. HF and dry the contents on hot plate. Extract the residue in 30 ml 6N HCl, boil and filter with 40 No. Whatman filter paper. Preserve the filtrate, ignite the residue in platinum crucible at 800°C. Take out the platinum crucible from furnace and fuse the residue with $K_2S_2O_7$ on burner. Dissolve the fused mass in the mother liquor and keep it on hot plate to reduce the volume till about 1 ml. and then add 50 ml. of 1N HCl in to it.

SEPARATION OF REE

Prepare a column of resin height 20 cm of 200-400 mesh, Biograd AG 50W x 8 H-form, conditioned in 1N HCl.

1. Load 50 ml of the above sample solution in the ion exchange column.
2. Elute it with 50 ml. 2N HCl and then 50 ml. 2N HNO_3 and discard the treated solution coming out from the column which will contain Na, Fe, Mg, Rb, Ca, Sr, Ba, etc.
3. Elute 2 times with 50 ml. 6N HNO_3 each time and collect the treated solution coming out from the column.
4. Elute 2 times with 50 ml. 8N HNO_3 each time and collect the treated solution coming out from the column.

Combine both (3 & 4) elutes (reated solution) and evaporate to dryness. Make the volume to 50 ml or 100 ml with 1% HNO_3 in a measuring flask and determine REE & Y in it with ICP (AES).

Regenerate the resin column by washing with 150 ml 1N HCl.

Rare earth element spectral lines for ICP analysis

Lanthanum. Recommended line – 398.85 nm

This is a sensitive element in the ICP, and also one of the more abundant in geological samples. It has several lines of almost equal sensitivity and there does not appear to be any clear evidence to show which lines are the best. The 398.85 line has been widely used and gives good results. It has a small interference from Ca but usually this is too small to be significant.

Cerium Recommended line – (418.66 nm)

This is almost invariably the most abundant rare earth element in geological samples and it is rarely necessary to measure at levels close to the detection limit. The 418.66 nm line has been used by several authors and good results obtained. It does suffer from interferences from Zr and Dy. Normally the levels of these elements are too low relative to Ce concentrations for the interferences to be significant. However, in a few rock samples with very high Zr values (5000 µg/g in the sample or more) the Zr may be eluted from the resin with the Ce. Here the interference corrections must be critically evaluated and possibly other Ce lines might be better.

Praesodymium-Recommended line (422.29 nm)

This line has minor spectral interferences from Ce and also Sr and Ca for which corrections can be made. Other spectral line (some of which have slightly better sensitivity) have been studied but appear to have more severe spectral interferences. Thus the adjacent 422.54 nm Pr line has a serious interference from Sm. Since the levels of Pr and Sm might well be comparable in geological samples such interference would be very difficult to correct.

Neodymium-Recommended line (430.36 nm)

This is a more abundant rare earth element and its determination should be relatively straightforward. The only interference of note on the 430.36 nm line is a very small interference from Ba and this is rarely significant. Good results are usually reported for Nd. However, for samples with Ba present at percent levels there could be problems. Ba (together with Sr and Sc) is one of the few elements that are not separated from the rare earth elements using the procedure described above.

Samarium-Recommended line 359.26 nm

Interferences from the two most abundant rare earths Ce or Nd (and sometimes both) cause serious problems for the selection of the 'best' line for Sm. On balance the most sensitive Sm line (359.26) is preferred although it too has a modest interference from Nd. The Sm 373.92 line is one of the few other Sm lines that could be used; it is free from Ce and Nd interference although it has some interference from Pr.

Europium-Recommended line 381.97 nm

The chondritic abundance of Eu is only 0.077 µg/g and it is therefore very fortunate that its detection limit in the ICP is quite exceptionally low. All authors appear in agreement that the 381.97 is the preferred line for analysis. It has trace interference from Nd but this is small enough to be readily corrected. There is also a very small interference from Fe that is not significant when the separation technique described above is used.

Gadolinium-Recommended line (335.05 nm)

The most sensitive line 342.25 nm has interference from Ce. The next most sensitive line is the 336.22 line, but this has Y interference. Another sensitive Gd line 376.85 has interference from both Ce and Nd. All these interferences would present serious problems for geological use. The line recommended (335.05) has a small Ca interference and Zr interference. Normally these will not present a serious problem when the separation method described above is used.

Dysprosium-Recommended line 353.17 nm

This is much the most sensitive line for Dy and appears to be almost entirely free from spectral interferences. There is a small interference from manganese but this would not be present using the separation technique outlined above. Excellent results are reported for this element.

Holmium-Recommended line 345.6 nm

This is the most sensitive Ho line and almost invariably used. The low concentration of Ho found in most geological samples make the use of this line almost obligatory. The only interference recorded is a very small Zr interference and this is rarely likely to be significant.

Erbium-Recommended line (390.63)

Erbium is a comparatively low abundance rare earth in geological samples. Thus it's sensitivity in the ICP is adequate. The 390.63 is only one of several lines than can be used and it does give reasonable results.

Ytterbium-Recommended line 328.94 nm

This line is the most sensitive, having no significant interferences and excellent results are obtained.

Lutetium-Recommended line 261.5 nm line

This line has excellent sensitivity and this enables good Lu values to be obtained in spite of its low abundance in geological samples. The 261.5 line is almost ten times more sensitive than the next most sensitive line; consequently its use is virtually obligatory. No serious interferences are recorded.

5.2 ANALYSIS OF PLATINUM GROUP ELEMENTS

Platinum group elements occur in most natural materials at very low concentrations and are very heterogeneously distributed so their determination almost invariably requires a separation and preconcentration step**.**

The names of Platinum Group Elements are given below:

1. **Ruthenium (Ru)**
2. **Rhodium (Rh)**
3. **Palladium (Pd)**
4. **Osmium (Os)**
5. **Iridium (Ir)**
6. **Platinum (Pt)**

To obtain the low detection limit upto ppb level, the preconcentration of PGE is very essential. Fire assay is the most common sample preparation procedure for PGE analysis. The basic reason for the continued use of this technique is that a large sample size can be treated (typically 25 gm, 50 gm or 100 gm), which is to some extent compensates for nugget effects during sub-sampling. Smaller sample sizes are generally considered to be inadequate for assessing low grade ores. Fire assay procedures vary considerably from laboratory to laboratory and their reliability depends to a large extent on the skill of the analyst, sample composition and the fusion flux mixture used.

Nickel sulphide fire assay is preferred to lead fire assay for multi-element analysis because it provides efficient collection for most of the noble metals. Only it is less effective for Au collection and hence lead fire assay is preferred for Au collection. Special technique is necessary to avoid the loss of volatile Os compounds (OsO_4) particularly at button dissolution stage.

The low detection limit upto 5 to 10 ppb is desirable while analyzing the PGE and suitable instruments like AAS (Graphite Furnace), ICP (AES) or ICPA (MS) are preferable.

To obtain the low detection upto ppb level, the preconcentration and separation of PGE is very essential**.**

PRECONCENTRATION PROCEDURE:

Since 1970s, the nickel sulphide collection procedure has been documented and used for the preconcentration of platinum group elements.

PROCEDURE

During the analysis all the reagents of recognized analytical grade are used unless otherwise specified and only distilled water or deionised water is used.

FUSION AND NICKEL-SULPHIDE BUTTON PREPARATION:

25 to 50 gms of sample (depending upon the PGE present) are taken on glazed sheet. The flux containing following reagent in proper proportion has been added to the sample.

Borax (anhydrous)	90 gms
Sodium Carbonate (anhydrous)	45 gms
Nickel Carbonate (LR Grade)	37 gms
Sulphur Powder (Commercial)	12 gms
Silica (LR Grade)	16 gms

The quantity of flux can be changed depending upon the mineralogy of the sample.

The flux is properly mixed with the sample. The mixture is transferred in a free clay pot and fused in the furnace at 1000^{o}C and the sample with flux is kept at this temperature for about 1 hr. 15 minute (75 minutes).

The pot is taken out from the furnace using a furnace tong while it is hot and melt is poured into an iron mould and allowed to cool.

When it is cooled the whole mass is taken out and nickel-sulphide button is taken out by breaking the slag. The slag is again fused in the same fire clay crucible using the flux having following proportion.

Borax	10 gms
Sodium carbonate	5 gms
Nickel carbonate	14.3 gms
Sulphur	3.5 gms

The whole mass is fused at 1200^{o}C in the furnace for an hour. The melted mass is poured in an iron crucible white it is hot and allowed to cool. When it is cooled the slag is removed and nickel-sulphide button is taken out. Both the buttons obtained are then crushed and ground to powder form using chromium pot in ring grinder mill (Avoid to grind using tungsten pot).

PREPARATION OF TEST SOLUTION

The crushed nickel sulphide sample is added in conical flask and 500 ml concentrate HCl is added to it. The flask is sealed using rubber cork and it is warmed on the hot plate at moderate heat at 130°C and the solution is aerated. So that the nickel-sulphide button is completely dissolved and clear dark green solution is obtained. Then H_2S gas through Kipp's apparatus is passed through the solution so that the entire nickel-sulphide button is dissolved. The solution is allowed to cool while passing H_2S through it.

The solution is filtered using 0.8 micron 47 mm dia Millipore filter paper under suction. The flask is rinse with dil. HCl till the filtrate is colourless. The flask is rinse and washed with distilled water.

The filter paper is placed in 150 ml beaker, 20 ml aqua regia is added and beaker is covered with watch glass. It is gently heated till the paper is decomposed. The solution is filtered using 40 No. Whatman filter paper. It is washed initially with dil. HCl and then with distilled water.

The filtrate in the beaker is evaporated on hot plate upto 1 to 2 ml. It is poured in 10 ml volumetric flask and diluted to 10 ml using distilled water (A).

The solution obtained (A) is coloured. Therefore, it is passed through Ion exchange column. (If the solution is colourless, then it is not necessary to pass through the Ion exchange column).

ION EXCHANGE COLUMN

The biored resins AG-50 W-X8 50 to 100 mesh size is gently heated with dil. HCl and filtered.

It is washed several times with water. A Dacron wool is placed at the bottom of column (50 ml capacity burette) and at the base the washed resin is added to it upto 10 cm height. Dacron wool is again kept under top of resin in the burette. The column is washed with water till the eluate has a pH equal to the water.

SOLUTION SEPARATION

The sample solution from the last step (A) is added in a beaker. 50 ml of 0.1 molar HCl and 0.2 molar HNO_3 is added and it is warmed to dissolve precipitated salt. It is allowed to cool and then passed through the column keeping the flow rate about one drop per second. The solution is collected in 400 ml beaker. The column is washed with 50 ml of distilled water. The volume of this solution is reduced keeping on hot plate. 2 ml of HCl and 3 ml of water is added to dissolve the residue and it is diluted in 10 ml volumetric flask upto the mark using distilled water.

This solution is used for the estimation of platinum group elements using ICP (AES).

PREPARATION OF CALIBRATION SOLUTION

The calibration solution is prepared as individual solution of each element or composite solution. The metal of each platinum group of elements used for preparing standard solution must be 99.99% pure and free from all contamination.

The instrumental conditions and the wavelength selected for each platinum group elements are as under:

Sl.No.	Name of Element	Wavelength in nm	Lower Detection Limit (ppm)
1.	Iridium	224.268	0.027
		212.681	0.030
		205.222	0.061
2.	Osmium	225.585	0.00036
		228.226	0.00063
		189.900	0.0012
3.	Palladium	340.458	0.044
		363.470	0.055
		229.651	0.068
4.	Platinum	214.423	0.030
		203.646	0.055
		204.937	0.071
5.	Ruthenium	240.272	0.030
		245.657	0.030
		267.376	0.036
6.	Rhodium	233.477	0.044
		249.077	0.057
		343.489	0.060
7.	Gold	242.795	0.0017
		267.595	0.031
		197.619	0.038

5.3 APPLICATION OF ICP-OES TO WATER ANALYSIS

Water is a valuable commodity even though it is abundant, and its quality in respect of dissolved or suspended material is of great importance in many areas. The effect of industrial pollution on the aqueous environment needs regular monitoring, and this in turn implies knowledge of the composition of the water, and the mode of entry and ultimate fate of any contaminants. In addition, industries are subject to legislative control on the quality of water they discharge into national water systems and sewers.

Being a liquid, water is already in the most favourable form for injection into the ICP. No chemical pretreatment beyond stabilization is required.

Again because of the low concentrations involved, interference effects from troublesome elements such as calcium, magnesium, aluminum, iron etc. are either negligible or can be dealt with very simply. Some of these elements, which are otherwise somewhat troublesome or expensive to determine, can be easily and very accurately dealt with by ICP for example, boron, sulphur, silicon and phosphorus.

Inductively coupled plasma emission spectrometry provides reliable information on chemical composition of natural waters. The four interdependent stages of sample collection, sample storage, laboratory analysis and data interpretation will all influence significantly the accuracy and precision of the final values obtained.

Advantages

- Samples in an ideal form for presentation
- Minor and trace element determinations possible simultaneously.
- Minimum chemical interference.
- Good data processing facilities.

Disadvantages

- High concentrations of some elements, e.g. Ca and Mg, may interfere with minor and trace element determinations.
- Suspended matter may block some nebulisers.
- Low sensitivity for some trace element.
- Spectral interferences must be overcome.

Calibration, Standard Solutions and Accuracy

The wide and nearly linear calibration range characteristic of the ICP permits calibration graphs covering several orders of magnitude in concentration to be used. Multi-elemental standard solutions should be planned and prepared with care. Thus, it is usual to group elements together having regard for purity of reagents, relative concentrations of analytes, spectral interferences, chemical compatibility and stability. The US National Bureau of Standards produces SRM 1643a, which is a synthetic solution certified for its trace element content.

This Standard Reference Material is intended primarily for evaluating the accuracy of trace element determinations in filtered and acidified fresh water and for calibrating instrumentation used in these determinations.

Wavelength Selection and Spectral Interferences

A typical wavelength program is used for water analysis on a simultaneous ICP fitted with a Nitrogen Generator. Problems can arise where a line of a major component lies close to a line used to detect a trace element. Variations in the intensity of the background signal can become critical in the accurate determination of trace elements in natural water matrices. A small shift in the background signal could generate a totally spurious value. Subtraction of spectra is a very useful tool in the interpretation of emission signals arising from analyte concentrations close to the detection limit.

WAVELENGTH FOR ICP JY 180 IN INDIAN BUREAU OF MINES LABORATORY

Elt	WV	Low Limit	High Limit
Ca	3179.33	0.2 mg/l	400 mg/l
Mg	2790.79	0.2 mg/l	300 mg/l
Na	5895.92	0.1 mg/l	2,500 mg/l
K	7664.9	0.3 mg/l	400 mg/l
Si	2516.11	0.5 mg/l	100 mg/l
Li	6707.76	0.1 mg/l	10 mg/l
Sr	4077.71	0.01 mg/l	10 mg/l
B	2496.78	20 µg/l	1 mg/l
Be	3130.42	5 µg/l	1 mg/l
Fe	2599.4	20 µg/l	100 mg/l
Mn	2576.1	5 µg/l	5 mg/l
Al	3082.15	20 µg/l	10 mg/l
Co	2286.16	2 µg/l	1 mg/l
Cr	2677.16	5 µg/l	10 mg/l
Cu	3247.54	2 µg/l	5 mg/l
Ni	2316.04	5 µg/l	5 mg/l
Zn	2138.56	5 µg/l	5 mg/l
Ag	3280.68	5 µg/l	1 mg/l
Cd	2265.02	2 µg/l	5 mg/l
As	1890.42	10 µg/l	1 mg/l
Ce	4186.6	5 µg/l	1 mg/l
La	4086.6	10 µg/l	1 mg/l
Mo	2020.32	10 µg/l	5 mg/l
Nb	3163.4	10 µg/l	1 mg/l
Pb	2203.53	2 µg/l	5 mg/l
Sb	2068.33	5 µg/l	1 mg/l
Se	1960.9	5 µg/l	1 mg/l
Sn	1899.89	5 µg/l	1 mg/l
Ti	3349.41	10 µg/l	5 mg/l
V	3102.3	10 µg/l	1 mg/l
W	2079.11	20 µg/l	5 mg/l
Y	3710.29	10 µg/l	1 mg/l
P	1782.87	50 µg/l	5 mg/l
Ba	4554.04	5 µg/l	5 mg/l

5.4 THE ICP-OES IN ENVIRONMENTAL APPLICATIONS

The ICP-OES is an efficient analytical process for the determination of inorganic pollutants in environmentally relevant matrices. The application of this technique has been scheduled as the standard method of analysis for water, waste water and sludge. The ICP-OES method is distinguished by the following advantageous qualities.

- Larger linear dynamic range (3-4 orders)
- Little chemical interference
- Higher sample throughput (particularly for simultaneous instruments)
- Lower Limits of Detection multi-element capabilities
- Small calibration expense (as a rule, 2 point calibration)
- High degree of automation

Interferences

ICP-OES can be regarded as an interference free method. Spectral Interferences can be eliminated only through accurate line selection and background correction. The chemical matrix effects are extraordinarily small for ICP-OES.

Applications in Environmental Analyses

ICP-OES is used for environmental analysis as given below:

1. **Waste water :** The standardization of the spectrometer occurs for all elements using a blank sample and a 1 mg/liter standard solution.

2. **Air particulates :** 250 mg of an air particulate sample were dissolved in 5 ml HNO_3 and 1 ml HF. The clear solution was diluted to 250 ml after filtration. The sample is analysed by using ICP.

3. **Sewage sludge :** The sewage sludge dissolution depends on the sewage sludge procedure with aqua regia. Because of the high content of alkali earth elements (particularly Ca) and Fe, it is convenient to dilute the sample and to make a matrix adjustment. The spectrometer was standardized with a blank sample and a 1mg/liter multi-element standard for Cd, Cr, Cu, Ni and Pb and with a 10 mg/liter standard for Zn.

It is important to note that the use of ICP-OES for determining environmental analysis and the results obtained are characterized as good with the certified values of SRM.

6. Methods of Analysis of Environmental Samples

6.1 DETERMINATION OF DISSOLVED FLUORIDE, CHLORIDE, NITRATE, ORTHOPHOSPHATE, SULPHATE IONS USING ION CHROMATOGRAPHIC METHOD

Determination of common ions such as fluoride, chloride, nitrate, phosphate, sulphate, etc., which are soluble in water can be analysed using various methods for individuals. But all above ions can be determined on a single ion chromatograph instrument.

Principle

A water sample is injected into a stream of carbonate-Bicarbonate eluent and passed through a series of ion exchangers. The ions of interest are separated on the basis of their relative affinities for a low capacity, strongly basic anion exchanger (guard & separator column). The separated anions are directed onto a strong basic cation exchanger (packed bed suppressor). In the suppressor the separated anions are converted to their highly conductive acid forms and carbonate-bicarbonate eluent is converted to weakly conductive carbonic acid. The separated anions in their acid forms are measured by conductivity and are identified on the basis of retention time as compared to standards and quantitatively calculated considering the peak area or peak height of the spectra.

Interferences

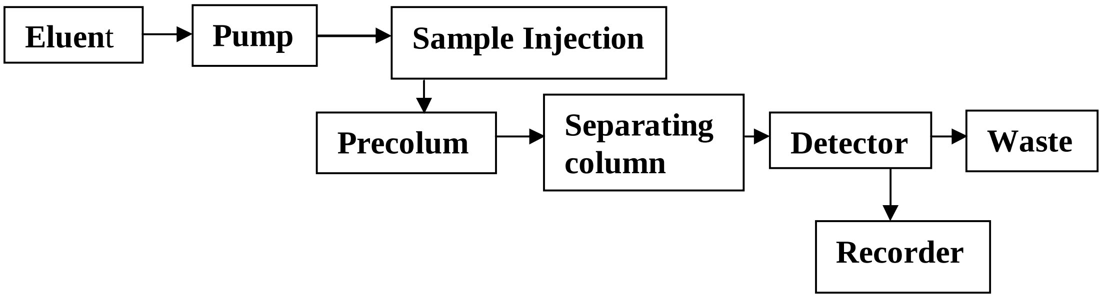
Substance that has a retention time coinciding with that of any anion to be determined will interfere such as low molecular weight organic acids interfere at high concentration for the determination of chloride and fluoride.

Reagents

- **i.** Distilled water filtered through 0.45 um fibre membrane filter.
- **ii.** **Eluent solution**: Sodium carbonate-sodium bicarbonate solution. Dissolve 1.0176 gm Na_2CO_3 (0.0024M Na_2CO_3) + 1.008 gm $NaHCO_3$ (0.003 M, $NaHCO_3$) in distilled water and dilute to 4000 ml with distilled water.
- **iii.** **Stock solutions of standard anions :** Prepare 1000 mg/l solution containing of each anions. F, Cl, NO_3, PO_4, SO_4, etc**.**
- **iv.** **Mixed standard solutions**: As per your requirements prepare standard solutions of different anion composition from the stock solutions. Use polyethylene vessels for storing of samples and standards.

COMPONANTS OF ION CHROMATOGRAPH APPARATUS

- Eluent Reservoir
- Pump having a very low pulsation effect
- Sample injection system (i.e. sample loop : 50 ml. solution)
- Precolumn
- Separating column with the required separating performance.
- Conductivity detector with or without a suppressor device.
- Recording device (i.e. integrator with plotter)



(Schematic Digram of Ion Chromatograph System)

Procedure

Set up Ion-Chromatograph instrument according to the manufacturers instructions.

Calibration

Identify the anions by comparing the retention times with those of the standard solutions. The retention time is dependant on concentration and matrix. The area of peak (or height) is proportional to the concentration of anion.

Prepare calibration and blank solutions and feed through Ion-Chromatograph establish the calibration function.

If the ion concentration of sample to be analysed exceeds the range of validity, dilute the sample. Sometimes, it may be necessary to establish a new calibration function for the lower concentration range.

Measurement of Sample Solutions

Filter the sample solution through 0.45 μ membrane filter to prevent adsorption of the anions and also prevent from contamination of sample.

Feed filtered sample through Ion-Chromatograph in a similar manner.

Calculations

Calculate the mass concentration in mg/l of anion in solution using the peak area or peak height according to the equation.

$$\text{Anion, mg/l} = \frac{C_i \times a_o}{bi}$$

Where C_i = measured value in terms of peak height, mm or peak area in l mm^2
b_i = slope of calibration function, mm.l/mg, mm^2/mg.
a_o = ordinate intercept of calibration function, mm or mm^2

6.2 ANALYSIS OF SODIUM & POTASSIUM IN WATER, WASTE WATER, EFFLUENTS, SOLIDS, SOILS ETC. USING FLAME PHOTOMETER

Sodium & potassium are normally found in water, wastewater, in solids and soils also. These can be analysed quantitatively using "Flame Photometer" at ppm to percentage levels.

PRINCIPLE OF FLAME PHOTOMETRY

Flame photometry is based on the fact that of alkali metals can be thermally excited in a low temperature flame and when the atoms return to the ground state they emit radiation which lies in the visible range of the spectrum. Each element emits a characteristic radiation at a wavelength specific to that element.

For example : Na = 589 nm, K = 766.5 nm.

Over a certain range of concentration the intensity of the emitted radiation is directly proportional to the number of atoms returning to the ground state. This in turn is proportional to the absolute quantity of species volatilised in the flame i.e. light emitted is proportional to the sample concentration at its characteristics wavelength is isolated by an optical filter and intensity of that light is measured by a photodetector which provides a signal proportional to the sample concentration.

Reagents

1. **Stock Sodium Chloride Solution** : Dissolve 0.2544 gm sodium chloride (AR) (NaCl) in water and dilute to 1000 ml with distilled water.

   1 ml = 100 mg/l = 100 ppm Na

2. **Stock Potassium Chloride Solution** : Dissolve 0.1910 gm potassium chloride (KCl) (AR) in distilled water and dilute to 1000 ml with distilled water.
   1 ml = 100 mg/l K = 100 ppm K

A. DETERMINATION OF SODIUM AND POTASSIUM IN LIQUID SAMPLES

i. **Standard sodium chloride solution** : Dilute 10 ml, 100 ppm Na solution to 100 ml with distilled water.

(1 ml = 10 ppm Na)

ii. **Standard Potassium chloride solution** : Dilute 10 ml, 100 ppm K solution to 100 ml with distilled water.

(1 ml = 10 ppm K)

- Prepare standard mixture of sodium and potassium taking suitable aliquots ranging from 0 to 10 ppm, Na & K in 100 ml volumetric flask and dilute up to the mark.
- Set up an instrument as per the manufacturer’s operation instructions.
- Feed the standard mixture solution of sodium and potassium into the instrument for standardization.

a. Determination of soluble sodium and potassium in liquid samples.

- Filter sample through Whatman No.40 filter paper (in case of removal of suspended solids).
- Take filtrate for the determination of soluble sodium and potassium in liquid sample.
- Feed above filtrate into the Flame Photometer which is standardized as per instructions.
- Find out the concentration obtained either from graph or directly from instrument itself.
- Calculate concentrations of sodium and potassium and express in mg/l.

b. Determination of total sodium and potassium in liquid samples.

- Take suitable aliquot of sample in 250 ml beaker.
- Add few drops of hydrochloric acid (in case of suspended solids are present) to dissolve suspended solids.
- Warm on hot plate if needed, cool.
- Filter through Whatman filter paper No.40, wash.
- Make up the volume to 100 ml with distilled water.
- Feed this filtrate in the Flame Photometer as usual manner.
- Calculate the concentrations of sodium and potassium and express in mg/l.

B. DETERMINATION OF SODIUM AND POTASSIUM IN SOLID SAMPLES

- Take 0.1-1 gm fine powdered sample in platinum crucible (wt. can be varied depending upon conc. of Na & K).
- Add 1-2 drops of con. Sulphuric acid so that all sample should be wet.
- Add 2-5 ml hydrofluoric acid.
- Evaporate to dryness on either hot plate or on burner.
- Extract residue with little volume of hydrochloric acid.
- Warm on hot plate for few minutes. Cool.
- Filter through Whatman filter paper No.40. Wash.
- Transfer filtrate in 100 ml volumetric flask and dilute to 100 ml with distilled water.
- Feed this solution in flame photometer as usual.
- Calculate the concentration of sodium and potassium and express in percentage or ppm**.**

6.3 DETERMINATION OF TURBIDITY IN WATER, WASTE WATER USING TURBIDITY METER/NEPHELOMETER

Turbidity in water/waste water is occurred due to presence of suspended matter. It can be measured using turbidity meter.

Principle

Turbidity is based on comparison of the intensity of light scattered by a sample with the intensity of light scattered by standard reference suspension under similar conditions.

Reagents

i. **Stock hydrazine sulphate solution** : Dissolve 1 gm hydrazine sulphate $(NH_2)_2.H_2SO_4)$ in water and dilute to 100 ml with distilled water.

ii. **Stock hexamethylene tetramine solution** : Dissolove 10 gms hexamethylene tetramine $\{(CH_2)_6 N_4)\}$ in distilled water and dilute to 100 ml with distilled water.

iii. **Standard mixture suspension solution** : Mix 5 ml of stock hydrazine sulphate solution and 5 ml of hexamethylene tetramine solution in 100 ml volumetric flask and dilute to 100 ml with distilled water.
(Turbidity of this solution = 400 NTU).

iv. For less than 400 NTU, dilute 10 ml 400 NTU solution to 100 ml in volumetric flask.
(Turbidity of this solution = 40 NTU).

Preparation of Standards

- Take suitable aliquots of standard suspension turbidity solution ranging from 0-40 NTU in 100 ml volumetric flasks and make up to the mark.
- Calibrate the instrument as per manufacturer's instructions.

Measurement of Turbidity in samples

Place the sample in absorbing tube of the meter and compare with the standards.
(Note – Dilution may be done in case of reading is out of calibration range)
Calculations :

$$NTU = \frac{A \ X \ (B+C)}{C}$$

Where A = NTU found in diluted sample
B = Volume of dilution water, ml
C = Sample volume taken, ml.

Interpretation of results

Turbidity readings may be reported as follows :

Reading Range NTU	Report to the nearest NTU
0-1.0	0.05
1-10	0.10
10-40	1
40-100	5
100-400	10
400-1000	50
>1000	100

6.4 DETERMINATION OF COLOUR IN WATER AND WASTEWATER (UV-SPECTROPHOTOMETRIC METHOD)

Colour may be due to presence of soluble ions in water such as iron and manganese or any other material by some activities.

Principle

Colour can be determined with comparing with that of known standards of colour units.

Reagents

Potassium chloroplatinate solution : Dissolve 0.2492 gm potassium chloroplatinate (K_2PtCl_6) and 0.2 gm cobaltous chloride ($CoCl_2.6H_2O$) in 10 ml conc. HCl and dilute to 100 ml with distilled water.

(1 ml = 1 mg Pt = 1000 μg Pt = 1000 Hazen)

Preparation of Standard Graph

- Take suitable aliquots of standard potassium chloroplatinate solutions ranging from 0-70 Hazen units in 100 ml volumetric flasks and dilute to 100 ml.
- Measure absorbance/transmittances at 288 nm.
- Plot standard graph between absorbance and hazen units.

Measurement of sample solutions

- Measure absorbance of sample directly at 288 nm.
- If absorbance exceeds 70 Hazen, sample solution is to be diluted accordingly so that absorbance should come in range of 70 Hazen units.

  (Note – In case of turbid solution, sample is to be centrifused to remove turbidity before taking absorbance).

6.5 DETERMINATION OF SUSPENDED SOLIDS, TOTAL SOLIDS, DISSOLVED SOLIDS, INORGANIC MATTER AND VOLATILE MATTER IN WATER, WASTE WATER, EFFLUENT ETC.

Water, wastewater, effluent etc. always contain solids either suspended or dissolved, may be organic or inorganic.

A. SUSPENDED SOLIDS

- Take suitable aliquot of the sample in which suspended solids is to be determined
- Filter through pre-weighed sintered glass crucible of G-4 porosity on vacuum pump.
- Keep sintered crucible in oven at 105°C for drying purpose.
- Weigh up to constant weight is obtained.

Calculations :

$$\text{S.S., mg/l} = \frac{\text{mg,S.S. (in aliquot) x 1000}}{\text{ml. aliquot of sample}}$$

if aliquot = 50 ml, then

$$\boxed{\text{S.S., mg/l} = \text{mg, S.S. (in aliquot)} \times 20}$$

B. TOTAL SOLIDS : (SUSPENDED SOLIDS + DISSOLVED SOLIDS)

- Take suitable aliquot of homogeneous sample in pre-weighed platinum dish.
- Keep on hot plate to evaporate completely
- Dry at 105°C.
- Weigh repeatedly up to constant weight is obtained.

$$\text{T.S., mg/l} = \frac{\text{mg, T.S. (in aliquot)} \times 1000}{\text{ml, aliquot.}}$$

If aliquot = 50 ml, then

$$\boxed{\text{T.S., mg/l} = \text{mg, T.S. (in aliquot)} \times 20}$$

C. DISSOLVED SOLIDS :

- Take suitable filtered (through Whatman No.40 filter paper) aliquot in platinum dish.
- Evaporate on hot plate
- Dry at 105°C
- Weight repeatedly up to constant weight obtained.

Calculations :

$$\text{D.S., mg/l} = \frac{\text{mg, wt (in aliquot)} \times 1000}{\text{ml. aliquot of sample}}$$

If aliquot = 50 ml, then

$$\boxed{\text{D.S., mg/l} = \text{mg, wt. (in aliquot)} \times 20}$$

D. TOTAL INORGANIC MATTER AND ORGANIC MATTER

- Take suitable aliquot of homogeneous sample in pre-weight platinum dish.
- Evaporate on hot plate

- Dry at 105^{o}C
- Take weight of dish and total solids up to constant weight.
- Ignite platinum dish along with solids on 550^{o}C in muffle furnace for half an hour.
- Take out dish, cool in desicator
- Weigh up to constant weight is obtained.

Calculations

a. Inorganic matter, mg/l= $\dfrac{\text{mg (wt. of residue) in aliquot after } 550^{o}\text{C x 1000}}{\text{ml, aliquot of sample}}$

b. Organic Matter, mg/l = $\dfrac{\text{mg, loss in mass after } 550^{o}\text{C x 1000}}{\text{ml. aliquot}}$

If aliquot = 50 ml, then

$$\boxed{\text{Mg/l = mg (in aluquot) x 20}}$$

E. DISSOLVED ORGANIC AND INORGANIC MATTER

- Take suitable aliquot of filtered (through Whatman No.40 filter paper) in pre-weighed platinum dish.
- Evaporate on hot plate.
- Dry at 105^{o}C in oven.
- Weigh repeatedly up to constant weight obtained.
- Ignite platinum dish along with solids obtained at 550^{o}C in muffle furnace for half an hour.
- Take out, cool in desicator.
- Weigh up to constant weight is obtained.

Calculations

Inorg.Matter, mg/l = $\dfrac{\text{mg. of residue after } 550^{o}\text{C x 1000}}{\text{ml. aliquot sample}}$

Org.Matter, mg/l = $\dfrac{\text{mg. mass loss at } 550^{o}\text{C x 1000}}{\text{ml. aliquot sample}}$

If aliquot = 50 ml, then

$$\boxed{\text{Mg/l = mg, (in aliquot) x 20}}$$

6.6 DETERMINATION OF CHEMICAL OXYGEN DEMAND IN WASTE WATER/EFFLUENT

Chemical Oxygen Demand (COD) test provides the oxygen required for the chemical oxidation of organic matter using a strong chemical oxidizing reagent.

Chemical Oxygen Demand determination has an advantage over BOD determination; the results can be obtained in 5 days while COD can be obtained within 5 hours. Moreover, the test is much easier, gives reproducible results and less effect of interferences as compared with B.O.D. test.

Principle

Organic matter present in sample gets oxidized quantitatively by Potassium Dichromate ($K_2Cr_2O_7$) in presence of sulphuric acid (H_2SO_4) added in excess. The excess potassium dichromate ($K_2Cr_2O_7$) remaining after the reaction is then titrated against ferrous ammonium sulphate solution $\{(Fe(NH_4)_2.SO_4)_2.\}$ The volume of potassium dichromate consumed for oxidation of organic matter gives the oxygen required for the reaction.

Reagents

i. **Standard potassium dichromate solution (0.25 N)** : Dissolve 12.259 gms $K_2Cr_2O_7$ in water and dilute to 1000 ml with distilled water.
ii. **Standard Ferrous Ammonium Sulphate Solution (0.25 N) :** Dissolve 97.5 gms. Ferrous Ammonium Sulphate $\{(Fe(NH_4)_2.(SO_4)_2.6H_2O)\}$ in 50 ml conc. H_2SO_4 and dilute to 1000 ml with distilled water.
iii. **Sulphuric acid reagent** : Dissolve 10 gm silver sulphate (Ag_2SO_4) in about 1000 conc. H_2SO_4 and keep for dissolution.
iv. **Ferroin Indicator** : Dissolve 1.485 gm 1-10-phenonthrolene + 0.695 gm Ferrous Sulphate ($FeSO_4.7H_2O$) in water and dilute to 100 ml with distilled water.
v. **Mercuric sulphate** : $HgSO_4$ (AR/GR).

Standardization of ferrous ammonium sulphate

- Take suitable aliquot of standard potassium dichromate solution in 250 ml beaker.
- Add about 15-20 ml conc. H_2SO_4.
- Dilute to about 100 ml with distilled water, Cool.
- Add 2-3 drops of Ferroin indicator.
- Titrate against ferrous ammonium sulphate solution. Change of blue-green colour to reddish brown shows the end point.

Calculation

$$N_{FAS} = \frac{ml, K_2Cr_2O_7 \text{ x } N\ K_2Cr_2O_7}{ml, F.A.S.\ consumed}$$

Procedure

- Take 0.4 gm $HgSO_4$ in 250 ml refluxing flask
- Add suitable aliquot of sample in the flask
- Add few glass bead to avoid bumbling/bumping
- Add excess 0.25N dichromate solution. (can be known by observing yellow colour of dichromate remain in the flask)
- Add about 30 ml conc. H_2SO_4 containing silver sulphate mix thoroughly.
- Place refluxing flask on heating mentles or on burner and reflux for about 2 hours.
- Stop heating; allow to cool, wash a condenser with distilled water.
- Transfer the content in 250 ml conical flask with careful washing.
- Dilute if necessary. Cool.
- Add 2-3 drops of Ferroin indicator.
- Titrate the excess dichromate against ferrous ammonium sulphate solution.
- Change of blue green colour to reddish brown shows the end point.
- Carry out the blank in a similar manner.

Calculations

$$COD,\ mg/l = \frac{(ml_b - ml_s) \text{ x } N_{FAS} \text{ x } 8000}{ml\ aliquot\ of\ sample}$$

Where ml_b =Volume of Ferrous Ammonium Sulphate required for blank.
ml_s =Volume of Ferrous Ammoninum Sulphate required for sample
N =Normality of Ferrous Ammonium Sulphate

If aliquot = 20 ml, then

$$\boxed{COD, mg/L = (ml_b - ml_s) \text{ x } N \text{ x } 50 \text{ x } 8}$$

$$\boxed{1\ ml\ 1\ N\ K_2Cr_2O_7 = 8\ mg\ COD}$$

(Note : (i) Ag_2SO_4 acts as a catalyst, (ii) $HgSO_4$ masks halides)

6.7 DETERMINATION OF BIOCHEMICAL OXYGEN DEMAND (BOD) IN WASTE WATER AND EFFLUENTS

Biochemical Oxygen Demand is defined as the amount of oxygen required by micro-organisms while stabilizing biologically decomposable organic matter in waste water, effluents under aerobic conditions. The test is carried out at 20°C for 5 days is considered as the standard. BOD provides a data for the determination of an efficiency of wastewater treatment procedures and pollution load of wastewater.

Normally two methods are used for the determination of BOD.

a. **Direct Method** : BOD is determined by measuring dissolved oxygen of waste water/effluent before and after incubation period of 5 days at 20°C.
b. **Seeded Dilution Method** : In seeded dilution method, dilute water is seeded with proper kind and number of organisms before the BOD test. It is important that a mixed group of organisms is called 'seed'. In absence of toxic substances all necessary nutrients such as nitrogen and phosphorous should be present.

Interference : Heavy metals & residual chlorine are commonly observed as interference in this process. Residual chlorine can be removed by the addition of equivalent amount of sodium sulphite solution.

Reagents

i. **Phosphate Buffer Solution (pH = 7.2) :** Dissolve 8.5 gms potassium dihydrogen phosphate (KH_2PO_4) 21.75 gms dipotasium hydrogen phosphate (K_2HPO_4) + 33.4 gms disodium hydrogen phosphate ($Na_2HPO_4.7H_2O$) 1.7 gm ammonium chloride (NH_4Cl) in water and dilute to 1000 ml with distilled water.
ii. **Magnesium sulphate solution (2.25%) :** Dissolve 22.5 gms Magnesium Sulphate ($MgSO_4.7H_2O$) in water and dilute to 1000 ml with distilled water.
iii. **Calcium chloride solution (2.75%)** : Dissolve 27.5 gms calcium chloride ($CaCl_2$) in water and dilute to 1000 ml with distilled water.
iv. **Ferric Chloride Solution (0.025%)** : Dissolve 0.25 gms ferric chloride ($FeCl_3.6H_2O$) in water and dilute to 1000 ml with distilled water.
v. **Sodium Sulphite Solution (0.025 N)** : Dissolve 1.575 gm sodium sulphite (Na_2SO_3) in water and dilute to 1000 ml with distilled water.
vi. **Potassium iodide (KI)** : Crystal (AR/GR)
vii. **Starch indicator:** (0.2%) solution.
viii. **Acetic acid** : Glacial acetic acid.

Procedure

A. Preparation of dilution water

a.

- Aerate the required volume of distilled water in a PVC container by bubbling compressed air for 1-2 days to attain saturation.
- Add 1 ml phosphate buffer
- Add 1 ml magnesium sulphate solution
- Add 1 ml calcium chloride solution
- Add 1 ml ferric chloride solution.
- Dilute to 1000 ml with aerated water and mix thoroughly

b. In case of waste water/effluent, which are not expected to have sufficient bacterial population, add 2 ml seed into dilution water. (Normally, 2 ml settled sewage is considered sufficient for 1000 ml dilution water).

c. Neutralise the sample to pH = 7 if it is highly alkaline or acidic accordingly.

d. Removal of residual chloride

- Take suitable aliquot of sample in 250 ml beaker/volumetric flask.
- Add 10 ml of 1:1 acetic acid solution.
- Dilute with distilled water if necessary
- Add about 1 gm KI solid (yellow colour appears if R-Cl_2 is present).
- Titrate the content against standard sodium sulphite (Na_2SO_3) solution using starch as an indicator.
- Calculate the volume of sodium sulphite required for aliquot taken.
- Add calculated volume/amount of sodium sulphite in aliquot sample taken for the determination of BOD.

e. If samples having high dissolved oxygen i.e. above 9 mg/l due to algal, reduce dissolved oxygen. by agitating the sample

f. Several dilutions of prepared sample are to be done so as to obtain about 50% depletion of Dissolved oxygen in dilution water but not less than 2 mg/l, dissolved oxygen.

g.

- Siphon out seeded dilution water in a volumetric flask/measuring cylinder half the required volume.
- Add required quantity of mixed sample solution.
- Dilute the desired volume by siphoning dilution water and mix thoroughly.

h. The following dilutions are suggested for better results.

For strong trade waste : 0.1% to 1%
Raw or settled sewage : 1% to 5%
Treated effluent : 5% to 15%
River Water : 25% to 100%

i. Siphon the dilution prepared as above in 4 labeled BOD bottles (300 ml capacity) and stopped immediately.

j. Keep one bottle for determination of initial dissolved oxygen and incubate 3 bottles at 20°C for 5 days.

(**Note** : Confirm that bottles have a water sealed)

k. Prepare a blank in duplicate by siphoning plain dilution water (without seed) to determine the oxygen consumption in dilution water.

l. Fix the bottles kept for immediate D.O. determination and blank.

- Add 2 ml $MnSO_4$ solution in each bottle.
- Add 2 ml Acid Reagent (500 gm NaOH + 150 gm KI +10 gm NaN_3 in 1 lit. D.M. water) (NaOH + KI + NaN_3) solution
- Determine D.O. in sample and in blank on initial day as usual manner.
- Determine D.O. in samples. Kept in incubator after 5 days at 20°C.

Calculations

Determine D.O. in the sample and in blank on initial day and after 5 days, when dilution water is not seeded:

BOD_5 mg/L = $(D_i - D_f) - (B_i - B_f)$ x decimal volumetric fraction of samples used

When dilution water is seeded:

BOD_5 mg/L =

$$(D_i - D_f) - (B_i - B_f) \times \frac{\text{Vol.of seed in diluted sample x decimal fraction of sample used}}{\text{Vol.of seed in seed control}}$$

Where D_i = D.O. of sample for initial day
D_f = D.O. of sample for final day (i.e. 5 day)
B_i = D.O. of blank for initial day
B_f = D.O. of blank for final day (i.e. 5 day)

6.8 DETERMINATION OF DISSOLVED OXYGEN IN WATER AND WASTEWATER

Oxygen is the most important for all living organisms, which is taken from air or taken from water in case of aquifers who consume dissolved oxygen in water/wastewater.

Dissolved oxygen can be analysed either using titrimetric method or using membrane electrode method.

TITRIMETRIC METHOD : IODOMETRIC AZIDE MODIFICATION METHOD

Principle :

In this process, manganous sulphate oxidized to manganous hydroxide (brown precipitate) in strong alkaline medium further iodine ions in an acidic solution, oxidized manganese reverts to its divalent state liberating of iodine equivalent to dissolved oxygen present in the sample. Liberated iodine is then determined by titrimetric method using sodium thiosulphate as a titrant and starch as an indicator.

Inference : NO_2-N and ferrous iron interefers, addition of KF solution before acidification, ferrous iron can be masked up to 200 mg/l.

Reagents

- **i.** **Manganous sulphate solution** : Dissolve 480 gms $MnSO_4.4H_2O$ or 400 gm $MnSO_4.2H_2O$ or 364 gm $MnSO_4.H_2O$ in distilled water and dilute to 1000 ml with distilled water.
- **ii.** **Alkali-iodide-azide solution** : Dissolve 500 gm NaOH or 700 gm KOH + 135 gm NaI (OR 50 gm KI) in distilled water + 10 gm NaN_3, mix & dilute to 1000 ml with distilled water.
- **iii.** **Sulphuric acid** : concentrated.
- **iv.** **Starch solution** : about 2% solution in boiling water.
- **v.** **Standard sodium thiosulphate solution (0.025 M).** Dissolve 6.205 gm $Na_2S_2O_3.5H_2O$ in distilled water, add 2-4 palletes of NaOH, mix and dilute to 1000 ml with distilled water.
- **vi.** **Standard potassium bi-iodate solution** : Dissolve 0.8124 gm $KH(IO_3)_2$ in distilled water and dilute to 1000 ml.
- **vii.** **Potassium fluoride solution** : (40%) : Dissolved 40 gm $KF.2H_2O$ in 100 ml distilled water.

STANDARDIZATION OF SODIUM THIOSULPHATE SOLUTION

- Take suitable aliquot of standard bi-iodate solution in 250 ml conical flask.
- Add about 2 gms of KI solid
- Add about 1 ml conc. H_2SO_4
- Dilute to about 100 ml with distilled water.
- Titrate liberated iodine against standard sodium thiosulphate solution using starch as an indicator. Disappearance of blue colour shows the end point.

$$\text{N sod.thio.} = \frac{\text{ml.aliquot (St.pot.bi-iodate) x N}}{\text{ml. (vol. of thio.sulphate)}}$$

DETERMINATION OF DISSOLVED OXYGEN

Procedure

- Take suitable volume (150 ml) of sample in 150 ml BOD bottle (Normally 300 ml full bottle sample is to be taken).
- Add 1 ml $MnSO_4$ solution (Note: tip of pipette should be below the surface of sample solution)
- Add 1 ml alkali-iodide-azide solution as above, mix well.
- Stand for few minutes to settle precipitate.
- Add 1 ml conc. H_2SO_4
- Mix the content by inverting the bottle several times till precipitate is completely dissolved.
- Take a suitable aliquot from above solution considering added reagents and loss of solution.
- For example if we take 100 ml aliquot we should take 101.5 ml for titration.
- Titrate against sod.thiosulphate solution using starch as an indicator as usual manner.

Calculations

$$\text{D.O., mg/L} = \frac{\text{ml(thio)} \times \text{N(thio)} \times 1000 \times 8}{\text{ml aliquot}}$$

If aliquot = 200 ml, then

$$\boxed{\text{D.O., mg/L} = \text{ml(thio)} \times \text{N(thio)} \times 5 \times 8}$$

Note: 1 ml, 1N thiosulphate = 8 mg D.O.

6.9 DETERMINATION OF PHENOLIC COMPOUNDS AS C_6H_5OH (DIRECT COLORIMETRIC METHOD)

Phenol (C_6H_5OH) is a hydroxy derivative of benzene. It may occur in industrial as well as in drinking water. During chlorination process it produces some peculiar objectionable taste and can be removed giving treatment with chloramines, ozonization, activated carbon adsorption etc.

Principle

Phenolic compounds react with 4-aminoantipyrine at pH about 8-10 in presence of pot. ferricyanide to form a coloured antipyrine dye which can be measured at 510 nm.

Interference :

Interferences can be eliminated using distillation method at the initial stage.

Reagents

i. **Stock phenol Solution :** Dissolve 0.10 gm phenol in distilled water and dilute to 1000 ml with distilled water.

(1 ml = 0.1 mg phenol = 100 μg phenol).

ii. **Standard phenol solution** : Dilute 10 ml, 100 μg phenol solution to 1000 ml with distilled water.

(1 ml = 1 μg phenol)

iii. **Ammonium chloride solution : (5%) :** Dissolve 5 gm NH_4Cl in water and dilute to 100 ml with distilled water.

iv **Ammonia solution :** Concentrated solution.

v. **Aminoantipyrine solution : (2%)** : Dissolve 2 gm 4-amino-antipyrine in distilled water & dilute to 100 ml with distilled water.

vi. **Potassium ferricyanide solution : (8%) :** Dissolve 8 gm potassium ferricyanide in water and dilute to 100 ml with distilled water.

PREPARATION OF STANDARD GRAPH:

- Take suitable aliquots from standard phenol solution from range of 0 to 10 mg/lit. phenol in 100 ml volumetric flask.
- Add 2 ml NH_4Cl solution in each volumetric flask mix.
- Adjust pH around 8-10 using ammonia solution, mix.
- Add 2 ml aminoantipyrine solution. Mix.
- Add 2 ml pot.ferricyanide solution mix again and dilute to 100 ml with distilled water. Mix thoroughly.
- Measure absorbances/transmittances at 510 nm. after 15 minutes.
- Carry out blank in a similar manner.
- Plot a standard graph between absorbance and concentrations of phenol.

PROCEDURE FOR WATER/ WASTEWATER/EFFLUENT SAMPLES

- Take suitable aliquot (without distillation) of sample in 100 ml. volumetric flask.
- Add 2 ml NH_4Cl solution. Mix.
- Adjust pH around 8-10 with ammonia solution. Mix.
- Add 2 ml aminoantipyrine solution. Mix again.
- Add 2 ml pot. ferricyanide solution. Mix and dilute to 100 ml with distilled water and mix thoroughly.
- Measure absorbance/transmittance at 510 nm after 15 minutes.

Calculations

$$\text{Phenol, } \mu g/L = \frac{\mu g \text{ phenol (in aliquot) x 1000}}{\text{ml, aliquot}}$$

If aliquot = 100 ml then

$$\boxed{\text{Phenol, } \mu g/L = \mu g \text{ phenol (in 100 ml) x 10}}$$

6.10 DETERMINATION OF OIL AND GREASE IN WATER AND WASTE WATER

Oil and grease are the material that dissolved in trichlorotrifluroethane in acidified solution along with sulphur compounds. Organic dyes, chlorophyls etc. It can be determined by gravimetric method.

Principle

Oil and grease are extracted with trichlorotrifluoroethane and separated from the aquous phase of sample. The extracted oil and grease present in trichlorotrifluoroethane is evaporated and the residue is weighed and reported as oil and grease.

Reagents

i. **Hydrochloric acid :** Dilute 1 : 1.
ii. **Sodium sulphate crystals (Na_2SO_4), (anhydrous)**
iii. **Trichlorotrifluoroethane :** boiling point 47°C.

Procedure :

- Take suitable aliquot in a separating funnel of suitable volume.
- Add about 2-5 ml dil. Hydrochloric acid, Mix.
- Add about 25-30 ml trichlorotrifluoroethane in the funnel.
- Shake gently for about 5-10 minutes.
- Allow to stand for separating into two layers.
- Run the trichlorofrifluoroethane layer in a platinum dish weighed previously.
- Again add 25-30 ml trichlorotrifluoroethane into the separating funnel.
- Shake for 5-10 minutes.
- Allow to stand for separating two layers.
- Drain the organic layer in the same dish.
- Place the dish either on water bath or in oven to dry or evaporation.
- Dry on 105-110°C for 10-15 minutes.
- Take weight after drying.
- Carry out blank.

Calculations

Deduct the blank mass, if any

$$\text{Oil \& Grease, mg/L} = \frac{\text{wt. of dish after drying} - \text{wt. of emply dish} \times 1000}{\text{ml, sample aliquot}}$$

if 1000 ml sample is taken, then,

$$\boxed{\text{Oil \& Grease, mg/L} = \text{Final wt. of dish} - \text{Initial wt. of dish}}$$

6.11 DETERMINATION OF SULPHATE IN WATER/WASTE WATER/EFFLUENT

Sulphate ions (SO_4^{-2}) occur in natural water and also in industrial waste. Sulphate compounds are easily soluble in water. Mine drainage wastes may contribute large amount of SO_4^{-2} through pyrite oxidation.

Two methods are described for the determination of sulphate.

a.TURBIDIMETRIC METHOD

Principle

Sulphate ion (SO_4^{-2}) is precipitated in an acidic medium with ($BaCl_2$) barium chloride so as to form ($BaSO_4$) barium sulphate crystal of uniform size and absorbance is measured at 420 nm comparing with standards.

Inferences

Colour and suspended solids in large amounts interfere. Suspended solids can be removed by filtering a sample solution.

Reagents :

- i. **Buffer solution :** Dissolve 30 gms magnesium chloride ($MgCl.6.H_2O$) + 5 gms sodium acetate ($CH_3COONa.3H_2O$) + 1 gm pot. nitrate (KNO_3) + 20 ml acetic acid in water and dilute to 1000 ml with distilled water.
- ii. **Barium chloride crystals.**
- iii. **Standard sulphate solution** : Dissolve 0.2219 gm Na_2SO_4 in distilled water and dilute to 1000 ml.

$$1 \text{ ml} = 0.1 \text{ mg } SO_4^{-2} = 100 \text{ ug } SO_4^{-2}$$

Preparation of Standard Graph

- Take suitable aliquots of standard sulphate solution ranging from 0-500 μg SO_4 in 100 ml volumetric flasks.
- Add 20 ml buffer solution in each flasks mix thoroughly.
- Add a pinch of barium chloride crystals ($BaCl_2$)
- Stir for about one minute
- Measure the absorbance/transmittances at 420 nm.
- Plot a standard graph between absorbance and concentrations of sulphate.

Measurement of sample solution

- Take suitable aliquot of filtered sample solution in 100 ml volumetric flask.
- Add 20 ml buffer solution, mix thoroughly.
- Add pinch of barium chloride crystals.
- Stir for about 1 minute.
- Measure absorbance/transmittance at 420 nm.
- Carry out blank in a similar manner.
- Find the concentration from standard graph.

Calculations

$$SO_4\text{, mg/l} = \frac{\text{mg } SO_4 \text{ in aliquot x 1000}}{\text{ml aliquot}}$$

if aliquot = 50 ml, then

$$\boxed{SO_4\text{, mg/l = mg, } SO_4 \text{ in 50 ml aliquot x 20}}$$

B. GRAVIMETRIC METHOD

Principle

Sulphate (SO_4^{-2}) is precipitated in hydrochloric acid (HCl) solution as ($BaSO_4$) barium sulphate by adding barium chloride ($BaCL_2$).

Interference

Commonly suspended solids are noticed as inference in this method and can be remove by filtering a sample solution before starting analysis.

Reagents

i. **Hydrochloric acid solution 1:1 diluted.**
ii. **Barium chloride solution (10%) :** Dissolve 10 gms barium chloride ($BaCl_2$) in 100 ml distilled water.

iii. **Methyl red indicator solution : (0.1%)** : Dissolve 0.1 gm methyl red in 100 ml distilled water.

iv. **Silver nitrate solution (1%)** : Dissolve 1 gm $AgNO_3$ in 100 ml distilled water.

(**Note** : Solution is used to check the presence of chloride ions in washings of $BaSO_4$ residue)

Procedure : Removal of Silica

- Take suitable aliquot of sample solution in 100 ml platinum dish.
- Add 1-2 ml hydrochloric acid.
- Evaporated to dryness.
- Ignite at 180°C to burn out organic matter if present.
- Extract residual mass with 2 ml hydrochloric acid. Boil and allow to cool and settle insolubles.
- Dilute to about 100 ml, boil and filter through Whatman No.40 filter paper after cooling.
- Take filtrate in 250 ml beaker.
- Adjust pH = 4-5 using methyl red indicator and adding hydrochloric solution.
- Add 2 ml hydrochloric acid in excess.
- Boil solution on burner.
- Mean time warm barium chloride solution also.
- Add about 5 ml barium chloride solution in boiling condition.
- Continue boiling for about 15 minutes to coagulate $BaSO_4$ precipitate.
- Allow to settle precipitate for over night.
- Filter barium sulphate through Whatman No.42 filter paper.
- Wash with hot water till absence of chloride ions. (can be checked by adding $AgNO_3$ solution, white precipitate appears if chloride ions present).
- Ignite residue (precipitate) of $BaSO_4$ at 900-950°C in muffle furnace.
- Weigh $BaSO_4$ mass up to constant weight obtained.

Calculations

$$SO_4\text{, mg/L} = \frac{\text{Wt. of } BaSO_4 \text{ (in aliquot) x 0.4116 x 1000}}{\text{ml aliquot of sample}}$$

if aliquot = 50 ml, then

$$\boxed{SO_4\text{, mg/l = mg, } BaSO_4 \text{ (in aliquot) x 0.4116 x 20}}$$

6.12 ANALYSIS OF SULPHIDE IN WATER AND WASTE WATER

Sulphide normally present in wastewater from the decomposition of organic matter or from industrial wastes and from the bacterial reduction of sulphate.

Sulphide forms H_2S which is toxic. It attacks metals and caused corrosion of concrete sewers because it is oxidized biologically to form H_2SO_4 on the pipe walls.

Determination of sulphide : Iodometric Method

Principle

Excess of standard iodine solution is added in the acidic media to get oxidize sulphide. Residual iodine is then titrated against standard sodium thiosulphate solution using starch as an indicator and sulphide is calculated accordingly.

Reagents

i. **Standard iodine solution : (0.01 N)** : Dissolve 10-15 gms KI in little distilled water, add 1.28 gms iodine crystals. Allow to dissolve completely, dilute to 1000 ml with distilled water. This solution should be standardized against standard sodium thiosulphate solution using starch as an indicator.
ii. **Standard sodium thiosulphate solution** :(0.01 N) Dissolve 2.482 gms sod.thiosulphate in distilled water and dilute to 1000 ml with distilled water.
iii. **Hydrochloric Acid solution** : 6 N.
iv. **Starch Solution :** Prepare about 5% with boiling water.

Standardization of iodine solution

- Take suitable aliquot of iodine solution in 250 ml conical flask.
- If necessary dilute with distilled water.
- Add 2 ml, 6N HCl solution, mix.
- Titrate against standard sodium thiosulphate solution, near the end point, add 2-3 ml starch solution and continue titration till blue colour disappears.

Calculation

$$\text{N (Iodine)} = \frac{\text{N (thio) x vol. of thio}}{\text{Vol..of iodine solution taken}}$$

Procedure for samples: Without precipitation with Zn

- Take suitable aliquot of iodine in 250 ml conical flask.
- If necessary dilute with distilled water.
- Add 2 ml, 6N HCl solution.
- Pipette out a suitable aliquot of the sample and discharge it under a surface of solution present in conical flask. Observe the colour of iodine which must be present at this stage, if not add more standard iodine solution so that colour of iodine remains (brown colour).
- Titrate the content of conical flask against standard sodium thiosulphate solution using starch as an indicator.

- Disappearance of blue colour shows the end point.

Calculations

$$S^{-2}\text{, mg/l} = \frac{\{(\text{ml Iodine x N Iodine}) - (\text{ml,thio x N thio})\} \text{ x } 16{,}000}{\text{ml.sample aliquot}}$$

(1 ml 1 N Iodine Solution = 16 mg S^{-2})

6.13 ANALYSIS OF SILICA IN WATER AND WASTE WATER

The silica (SiO_2) content in natural water is found in various concentrations. Silica in water is undesirable component for a number of industrial uses because it forms silica and silicate scale, which is very difficult to remove.

A. DETERMINATION OF SILICA USING SPECTROPHOTOMETRIC METHOD

Principle

In acidic pH, ammonium molybdate reacts with silica forming molybdosilicic acid gives yellow colour which further treated with reducing agent amino-2-naphthol-4-sulphonic acid forming blue colour and can be measured at 690 nm.

Interference

Colour, turbidity, sulphide & phosphate interfere. Colour and turbidity can be removed using aluminium hydroxide suspension solution and treatment, while phosphate can be removed by treatment of oxalic acid solution.

Reagents

i. **Ammonium molybdate solution: (10% solution)**: Dissolve 10 gm $(NH_4)_6Mo_7O_{24}.4H_2O$ in distilled water and dilute to 100 ml with distilled water.
ii. **Oxalic acid solution: (7.5% solution):** Dissolve 7.5 gms oxalic acid ($C_2H_2O_4.H_2O$) in distilled water and dilute to 100 ml with distilled water.
iii. **Reducing agent solution:** Dissolve 0.50 gm amino-2-naphthol-4-sulphanic acid. Add 1 gm sod.sulphite (Na_2SO_3) in 50 ml distilled water, warm, prepare 30 gm $NaHSO_3$ solution in 150 ml distilled water and mix both. Filter in polythene bottle.
iv. **Sodium bicarbonate : Powder**
v. **Hydrochloric acid : 1:1 diluted**
vi. **Sulphuric acid: 1 N solution.**
vii. **Stock silica solution: D**issolve 0.4734 gm sod. Metasilicate nonanhydrous ($Na_2SiO_3.9H_2O$) in distilled water and dilute to 1000 ml with distilled water.
1 ml = 100 μg SiO_2 = 46.67 μg.Si

viii. **Standard silica solution:** Dilute 10 ml, 100 μg SiO_2 solution to 100 ml with distilled water (1 ml = 10 μg SiO_2 = 4.676 μg Si)

Preparation of standard graph

- Take suitable aliquots of standard silica solution ranging from 0-10 μg SiO_2 in 100 ml volumetric flasks.
- Add 1 ml (1:1) hydrochloric acid solution in each volumetric flask. Mix.
- Add 2 ml ammonium molybdate solution, Mix.
- Add 1.5 ml oxalic acid solution. Mix again.
- Add 2 ml reducing agent solution, mix and dilute to 100 ml with distilled water. Mix thoroughly.
- Measure the absorbance at 690 nm after 10 minutes.
- Plot a graph between absorbance and concentrations.

Determination of silica in samples

- Take suitable aliquot of the sample in 100 ml volumetric flask.
- Add 1 ml (1:1) hydrochloric solution. Mix.
- Add 2 ml ammonium molybdate solution. Mix.
- Add 1.5 ml oxalic acid solution. Mix.
- Add 2 ml reducing agent solution, mix, dilute to 100 ml with distilled water. Mix thoroughly.
- Measure absorbance at 690 nm after 10 minutes.
- Carry out blank in a similar manner.

Calculations

$$SiO_2,\ \mu g/l = \frac{\mu g\ SiO_2 (\text{in aliquot}) \times 1000}{\text{ml aliquot}}$$

If aliquot = 50 ml, then

$$\boxed{SiO_2,\ \mu g = \mu g\ SiO_2\ (\text{in } 50\text{ ml}) \times 20}$$

B. DETERMINATION OF SILICA BY GRAVIMETRIC METHOD

Principle

Decomposition of silica in presence of HCl and then dehydration by drying the sample and extraction with dil. HCl, residue which contains crude silica after ignition at

900-950°C, followed by hydrofluorization in presence of H_2SO_4, again igniting at 900-950°C and the difference can be obtained by weighing procedure in this process.

Reagents

- i. **Dilute/con. Hydrochloric acid.**
- ii. **Conc. sulphuric acid.**
- iii. **Hydrofluoric acid (40%).**

Procedure

- Take suitable aliquot of sample in 250 ml beaker.
- Add 10-15 ml hydrochloric acid.
- Keep a beaker on hot plate.
- Allow to evaporate and dry the sample
- Allow to cool and add 10-15 ml hydrochloric acid.
- Boil the content for 10 minutes.
- Cool the content.
- Filter through Whatman filter paper.
- Wash residue with hot water for 2-5 times.
- Place the residue in platinum crucible along with a filter paper.
- Ignite at 900-950°C for ½ an hour (in furnace).
- Take out the crucible, allow to cool and weigh the ignited residue.
- Add 1-2 drops of sulphuric acid in the platinum crucible so that residue becomes wet.
- Add 5-6 ml hydrofluoric acid.
- Place platinum crucible on low flame burner or on hot plate and allow to evaporate to dryness.
- Take out the platinum crucible and ignite at 900-950°C for 2-5 minutes.
- Allow to cool.
- Take weight of remaining residue.

Calculations

Wt. of SiO_2 = Weight of crucible before HF – Wt. of crucible after HF.

$$SiO_2\ \mu g/l = \frac{\mu g\ SiO_2(\text{in aliquot}) \times 1000}{\text{ml aliquot}}$$

If aliquot = 50 ml, then

$$\boxed{SiO_2,\ \mu g = \mu g\ SiO_2\ (\text{in 50 ml}) \times 20}$$

6.14 ANALYSIS OF PHOSPHOROUS IN WATER AND WASTE WATER

Various forms of phosphorous are found in water and waste water. Phosphorous is essential constituent of nutrient for growth of plants. It can be determined by colorimetry at the low level.

6.14.1 DETERMINATION OF PHOSPHOROUS BY STANNOUS CHLORIDE METHOD (SOLUBLE PHOSPHATE)

Principle

A blue colour is developed as molybdophosphoric acid in presence of stannous chloride as a reducing agent, which can be measured at 690 nm.

Reagent

i. **Ammonium molybdate solution:** Dissolve 25 gm ammonium molybdate $\{(NH_4)_6 Mo_7)_{24}.4H_2O)\}$ in 150 ml distilled water. Add 280 ml conc. H_2SO_4, allow to cool and dilute to 1000 ml with distilled water.

ii. **Stannous chloride solution**: Dissolve 2.5 gm $SnCl_2$ in 100 ml glycerol by heating on water bath with constant stirring.

iii. **Stock phosphate solution**: Dissolve 0.439 gm KH_2PO_4(AR) in distilled water and dilute to 1000 ml with distilled water. (1 ml = 100 μg PO_4).

iv. **Standard phosphate solution**: Dilute 10 ml, 100 μg PO_4 solution to 100 ml with distilled water in volumetric flask. (1 ml = 10 μg PO_4).

Preparation of standard graph

- Take suitable aliquots from standard phosphate solution in the range of 0-10 μg PO_4 in 100 ml volumetric flask.
- Add 4 ml ammonium molybdate solution in each flask, mix.
- Add 0.5 ml stannous chloride solution, mix again.
- Dilute to 100 ml with distilled water, mix thoroughly.
- Measure absorbances/transmittances at 690 nm after 10 minutes.
- Carry out blank in a similar manner.
- Plot a graph between concentrations and absorbances/transmittances.

Procedure for samples

- Take suitable aliquot of sample in 100 ml volumetric flask. (If turbidity present, filter through 0.45 um filter).
- Add 4 ml ammonium molybdate solution, mix.
- Add 0.5 ml stannous chloride solution, mix well.
- Dilute to 100 ml with distilled water and mix thoroughly.
- Measure absorbance/transmittance at 690 nm after 10 minutes.
- Carry out blank in a similar manner.

Calculations :

$$P, \mu g/l = \frac{\mu g\ P(\text{in aliquot}) \times 1000}{\text{ml, aliquot}}$$

If aliquot = 50 ml, then

$$\boxed{P, \mu g/l = \mu g\ P\ (\text{in 50 ml}) \times 20}$$

$$\boxed{P \times 3.06 = PO_4} \quad \text{OR} \quad \boxed{\frac{PO_4}{3.06} = P}$$

(**Note** : In case of coloured samples, treat with aluminium hydroxide suspension to decolorise and then proceed usually)

6.14.2 DETERMINATION OF PHOSPHOROUS BY ASCORBIC ACID METHOD (Soluble Phosphate)

Principle

Ammonium molybdate reacts with potassium antimonyl-tartrate in acid medium to give phosphomolybdic acid which is blue in colour and can be measured at 880 nm.

Reagents

i. **Potassium antimonyl-tartrate solution:** Dissolve 0.2743 gms potassium antimonyl-tartrate {$K(SbO)\ C_4H_4O_6.2H_2O$} in water and dilute to 100 ml with distilled water.

ii. **Ascorbic Acid Solution: (0.01 M)**: Dissolve 1.76 gm ascorbic acid in 100 ml flask & dilute to the mark.

iii. **Ammonium molybdate solution:** Dissolve 4 gm ammonium molybdate ($(NH_4)_6\ Mo_7O_{24}.4H_2O$) in water and dilute to 100 ml with distilled water.

iv. **Sulphuric acid solution: (5N)**: Dilute 14 ml conc. H_2SO_4 to 100 ml with distilled water.

v. **Combined Reagent Solution**

   a. Take 50 ml 5N H_2SO_4 solution in 100 ml flask.
   b. Add 5 ml potassium antimonyl tartrate solution, mix.
   c. Add 15 ml ammonium molybdate solution, mix.
   d. Add 30 ml ascorbic acid solution, mix thoroughly. Allow to stand for few hours to stabilize the mixture (mixture to be prepared feshly).

vi. **Stock phosphate solution**: Dissolve 0.439 gm KH_2PO_4(AR) in distilled water and dilute to 1000 ml with distilled water. (1 ml = 100 μg PO_4).

vii. **Standard phosphorous solution:** Dilute 10 ml, 100 μg, PO_4 solution to 100 ml volumetric flask. (1 ml = 10 μg PO_4).

Preparation of standard graph

- Take suitable aliquots of standard phosphate solution ranging from 0-10 μg PO_4 in 100 ml volumetric flasks.
- Add 8 ml combined reagent solution in each flask.
- Dilute to 100 ml with distilled water, mix thoroughly.
- Measure absorbances/transmittances at 880 nm. after 10 minutes.
- Carry out blank in a similar manner.
- Plot a graph between concentrations and absorbance.

Procedure for samples

- Take suitable aliquot of sample in 100 ml volumetric flask.
- Add 8 ml combined reagent solution, mix.
- Dilute to 100 ml with distilled water.
- Take absorbance at 880 nm after 10 minutes.Carry out blank in a similar manner.

Calculations:

$$\text{P, } \mu g/l = \frac{\mu g \text{ P(in aliquot)} \times 1000}{\text{ml, aliquot}}$$

If aliquot = 50 ml, then

$$\boxed{\text{P, } \mu g/l = \mu g \text{ P (in 50 ml)} \times 20}$$

Note: for the determination of total phosphate, sample is to be treated with HCl + HNO_3 upto dryness. Extract with water and proceed as usual).

6.15 ANALYSIS OF NITRITE NITROGEN (NO_2-N) IN WATER AND WASTE WATER

Nitrite is another form of nitrogen generally found in water and waste water sample in small quantity and can be analysed through formation of reddish purple azo dye at pH 2-2.5 using sulphanilamide & N-(1-naphthyl)-ethylenediamine hydrochloride at 520 nm.

Reagents

i. **α-naphthylamine hydrochloride solution:** Dissolve 0.6 gm naphthylamine in 1 ml hydrochloric acid and dilute to 100 ml with distilled water.
ii. **Sulphanilic acid solution:** Dissolve 0.6 gm sulphanilic acid in about 70 ml hot water. Add 20 ml conc. hydrochloric acid dilute to 100 ml with distilled water.
iii. **Sodium acetate buffer solution:** Dissolve 27.2 gms. Sodium acetate in water and dilute to 100 ml.
iv. **EDTA Solution:** Dissolve 0.5 gm EDTA in distilled water, add one pallet of NaOH and dilute to 100 ml with distilled water.
v. **Stock Nitrite Solution:** Disolve 0.4929 gm $NaNO_2$(AR) in water and dilute to 1000 ml with distilled water. (1 ml = 100 μg NO_2-N).
vi. **Standard Nitrite Solution:** Dilute 10 ml, 100 μg NO_2 solution to 1000 ml with distilled water. (1 ml = 1 μg NO_2-N).
OR dilute 1 ml, 100 μg NO_2-N solution to 100 ml. with distilled water (1 ml = μg NO_2-N)

Preparation of standard graphs

- Take suitable aliquots from the standard stock solution of NO_2 in the range of 0-10 μg NO_2-N in 100 ml volumetric flask.
- Add 2 ml EDTA solution in each of the volumetric flasks.
- Add 1 ml sulphanilic acid solution, mix well and allow to stand for 3-5 minutes.
- Add 1 ml α-naphthylamine hydrochloride solution.
- Add 1 ml sod.acetate buffer and dilute to 100 ml with distilled water and mix thoroughly.
- Measure absorbances/transmittances of each solution at 520 nm.
- Carry out blank in similar manner
- Plot a graph between concentrations against absorbances.

Procedure for samples

- Take suitable aliquot from the sample in 100 ml volumetric flask.
- Add 2 ml EDTA solution, mix.
- Add 1 ml sulphanilic acid solution, mix again.
- Add 1 ml α-naphthylamine hydrochloride solution.
- Add 1 ml sod.acetate solution and dilute to 100 ml with distilled water, mix thoroughly.
- Measure absorbance at 520 nm.

Calculations:

$$NO_2\text{-N}, \mu g/l = \frac{\mu g\ NO_2\ \text{(in aliquot)}\ \times 1000}{\text{ml, aliquot}}$$

If aliquot = 50 ml, then

$$\boxed{NO_2\text{-N}, \mu g/l = \mu g\ NO_2\text{-N(in 50 ml)} \times 20}$$

$$\boxed{N \times 3.29 = NO_2}$$

6.16 ANALYSIS OF NITRATE NITROGEN (NO_3-N) IN WATER AND WASTE WATERS

NO_3 is one of the compounds of nitrogen family and found in water and wastewater. It can be determined using spectrophotometer in the range of ultraviolet and visible too.

6.16.1 Determination Of Nitrate Nitrogen (No_3-N) In Visible Range At 410 Nm

Principle

In alkaline condition, nitrate gives yellow colour with phenol disulphonic acid solution, which can be measured at 410 nm and compared with standards.

Reagents

i. **Phenol disulphonic acid solution:** Dissolve 25 gms phenol in 150 ml conc. sulphuric acid. Heat for 2 hours, cool and store in coloured bottle.
ii. **Potassium permanganate solution: (0.05 N):** Dissolve 0.2 gm $KMnO_4$ in water and dilute to 1000 ml with distilled water.
iii. **Standard silver sulphate solution:** Dissolve 4.4 gm Ag_2SO_4 in distilled water and dilute to 1000 ml distilled water. (1 ml = 1 mg Cl.)
iv. **Oxalic acid solution: (0.05N)**: 0.265 gm/100 ml.
v. **Ammonia solution:** 30% solution.
vi. **Nitrate stock solution** : Dissolve 0.7218 gm KNO_3(AR) in distilled water and dilute to 1000 ml. (1 ml = 0.1 mg NO_3-N = 100 μg NO_3-N)
vii. **Standard nitrate solution:** Dilute 10 ml, 0.1 mg NO_3-N solution to 100 ml with distilled water. (1 ml = 10 μg NO_3-N).

Preparation of standard graph

- Take suitable aliquots from the standard NO_3-N solution ranging from 0 to 10 μg NO_3-N in 100 ml volumetric flask.
- Add calculated ml of Ag_2SO_4 solution (before this take aliquot of sample and determine equivalent of chlorine if present in sample by precipitating chloride as (Ag Cl) and warm.
- If precipitate is formed, filter through Whatman No.40 filter paper.

- Add 2-5 drops of $KMnO_4$ solution to remove nitrites if present.
- Remove excess $KMnO_4$ colour by adding oxalic acid dropwise till colour disappears.
- Add 2 ml phenol disulphonic acid solution.
- Adjust pH to around 7 by using ammonia solution, mix thoroughly and dilute to 100 ml with distilled water.
- Measure absorbances/transmittances at 410 nm.
- Plot a graph between concentrations and absorbances.

Determination of nitrate-nitrogen (NO_3-N)

- Take suitable aliquot of sample in 250 ml beaker.
- Add calculated volume of Ag_2SO_4 solution (equivalent to chloride) to precipitate chlorides as AgCl. Warm the solution, cool and filter through Whatman No.40 filter paper.
- Add 3-5 drops of $KMnO_4$ solution to remove nitrite if present in sample.
- Remove excess $KMnO_4$ by adding oxalic acid solution dropwise.
- Keep the beaker on water bath and allow to evaporate to dryness. Remove beaker and allow to cool.
- Add 2 ml phenol disulphonic acid solution and extract with about 25-30 ml distilled water.
- Adjust the pH around 7 by adding ammonia solution and make up to 100 ml with distilled water.
- Measure the absorbance/transmittance at 410 nm.

Carry out blank in a same manner.

Calculations:

$$NO_3\text{-N}, \mu g/l = \frac{\mu g\ NO_3 \text{ (in aliquot) } \times 1000}{\text{ml, aliquot}}$$

If aliquot = 50 ml, then

$$\boxed{NO3\text{-N}, \mu g/l = \mu g\ NO_3\text{-N(in 500 ml)} \times 20}$$

(**Note :** In case of coloured sample, treat aliquot with aluminium hydroxide suspension to remove colour).

6.16.2 Determination of Nitrate Nitrogen (No_3-N) In Ultra Violet Region Of Spectrophotometer At 220 Nm & 275 Nm

The method is applicable in case of clear drinking water where organic material is in less quantity. In acidic condition (in HCl) the measurements are carried out at 220 nm and at 275 nm.

Absorbance at 220 contributes the concentration of nitrate and organic material while at 275 nm absorbance due to only organic material. The method is purely impirical. Suspended solids are removed by filtration while addition of hydrochloric acid prevents from hydroxides and carbonates.

Preparation of standard graph

Reagents

i. **Hydrochloric acid:** 1N.
ii. **Stock Nitrate Nitrogen (NO_3-N) solution**: Dissolve 0.7218 gm KNO_3(AR) in water and dilute to 1000 ml with distilled water (1 ml= 100 µg NO_3-N).
iii. **Standard Nitrate Nitrogen (NO_3-N) solution:** Dilute 10 ml, 100 µg NO_3-N solution to 100 ml with distilled water. (1 ml = 10 µg NO_3-N).

Procedure

- Take suitable aliquots of NO_3-N solution ranging from 0-10 µg NO_3-N in 100 ml volumetric flask.
- Add 2 ml 1 N HCl solution, in each flask mix thoroughly.
- Measure absorbances/transmittances at 220 nm and 275 nm respectively.
- If absorbance at 220 nm = A and absorbance at 275 nm = B.
- Then, absorbance for NO_3-N = A – 2B.
- Plot standard graph between absorbances as calculated above against the concentrations.

Procedure for samples

- Take suitable aliquot of sample in 100 ml volumetric flask.
- Add 2 ml, 1N hydrochloric acid, mix thoroughly (remove turbidity if any by filtering before addition of hydrochloric acid solution).
- Dilute to 100 ml with distilled water, mix thoroughly again.
- Measure absorbances at 220 nm and 275 nm.

Calculations:

$$\text{Abs}_{220\text{ nm}} - 2\text{Abs}_{275\text{ mm}} = \text{Abs } (NO_3\text{-N})$$

$$NO_3\text{-N, µg/l} = \frac{\text{µg } NO_3\text{-N(aliquot) x } 1000}{\text{ml, aliquot}}$$

If aliquot = 50 ml, then

$$\boxed{\text{NO3-N, µg /l} = \text{µg } NO_3\text{-N (in aliquot) x } 20}$$

$$\boxed{\text{N x } 4.43 = NO_3}$$

6.17 ANALYSIS OF AMMONICAL NITROGEN (NH_3-N) IN WATER ANDWASTE WATER

In natural as well as in wastewaters ammonia is generated due to the microbiological activities of mostly organic nitrogeneous matter.

Principle

Alkaline Nessler's reagent reacts with ammonia present in water/waste water and develops a yellow colour compound, which can be measured at 410 nm.

Reagents

i. **Nessler's Regaent: (a)** Dissolve 100 gms mercuric iodide (HgI_2) and 70 gms potassium iodide (KI) in distilled water**. (b)** Dissolve 160 gms. Sodium hydroxide in water and mix with solution of (HgI_2+KI) prepared above. **(c)** Allow to stand for overnight. Filter if precipitate is formed. Keep clear solution in coloured bottle.
ii. **Zinc Sulphate Solution (10%)**: Dissolve 10 gm $ZnSO_4.7H_2O$ in distilled water and dilute to 100 ml with distilled water.
iii. **Sodium Hydroxide Solution (6N) :** Dissolve 240 gms NaOH in distilled water and dilute to 1000 ml with distilled water.
iv. **EDTA Solution:** Dissolve 50 gms EDTA and 10 gms NaOH in water and dilute to 100 ml with distilled water.
v. **Stock Ammonium Solution :** Dissolved 0.3819 gm NH_4Cl (AR) in water and dilute to 1000 ml with distilled water (1 ml = 0.1 mg N = 0.122 mg NH_3).
vi. **Standard Ammonium solution:** Dilute 10 ml stock solution to 1000 ml with distilled water. (1 ml = 1 μg N = 1.22 μg NH_3).

Preparation of standard graph

- Take suitable aliquots of standard ammonium solution i.e. from 0 to 10 μg N in 100 ml beaker.
- Add 1 ml zinc sulphate solution in each beaker, mix.
- Add 0.5 ml NaOH solution to attend a pH around 10, mix again.
- Allow to settle the precipitate.
- Filter through Whatman No.42 filter paper.
- Add 1-2 drops of EDTA solution, in filtrate, mix.
- Add 2 ml Nessler's reagent, mix thoroughly and dilute to 100 ml with distilled water.
- Measure absorbance/transmittances at 410 nm.
- Plot a graph between concentration and absorbance/transmittances.

Procedure for samples

- Take suitable aliquot of the sample in 250 ml beaker.

- Add 1 ml $ZnSO_4$ solution, mix.
- Add 0.5 ml NaOH solution, mix again.
- Allow to settle precipitate.
- Filter through Whatman No.42 filter paper.
- Add 1-2 drops of EDTA in the filtrate, mix.
- Add 2 ml Nessler's reagent solution, mix thoroughly and dilute to 100 ml with distilled water.
- Measure absorbance/transmittance at 410 nm.

Calculations :

$$NH_3\text{-N}, \mu g/L = \frac{\mu g\ NH_3\text{-N x (in aliquot) x 1000}}{\text{ml, aliquot}}$$

If aliquot = 50 ml, then

$$\boxed{NH_3\text{-N}, \mu g/L = \mu g\ NH_3\text{-N (in 50 ml) x 20}}$$

OR

$$\boxed{NH_3\text{-N x 1.21} = NH_3} \qquad \boxed{\frac{NH_3}{1.21} = N}$$

6.18 ANALYSIS OF RESIDUAL CHLORINE IN WATER AND WASTEWATER SAMPLES

To supply a good quality of drinking water in view point of health, chlorination is essential. As the process of chlorination destroy the disease producing bacteria i.e. micro-organisms. The chlorination procedure has some adverse effects also. During this process the chances of the formation of chloroform, which is harmful to the health. To minimize any adverse effects, it is essential that proper testing procedures to be adopted.

Various methods are available for the determination of residual chlorine. Iodometric method is adopted in I.B.M. laboratory.

Principle

At acidic pH, chlorine liberates equivalent amount of iodine with addition of pot.iodide, which can be determined after titration against standard sod.thiosulphate solution using starch as an indicator.

Interference

Organic sulphides and manganese, ferric and nitrite ions interfere along with some forms of combined chlorine. At acidic pH the effect of interfering parameters is minimized. Acetic acid is preferably used while titrating with sod.thiosulphate solution.

Reagents

i. **Standard Sodium Thiosulphate Solution: (0.01N)**: Dissolve 2.5 gms sod.thiosulphate (AR) $Na_2S_2O_3.5H_2O$ in distilled water and dilute to 1000 ml.
ii. **Standard potassium dichromate solution (0.01N) :** Dissolve 0.49 gm $K_2Cr_2O_7$ in distilled water and dilute to 1000 ml distilled water.
iii. **Starch solution:** Dissolve 5 gm starch in 100 ml boiling water.
iv. **Potassium iodide :** Crystals (AR)
v. **Sulphuric Acid:** 1:1 dilute.

Procedure: Standardization of Sod.Thiosulphate

- Take 25 ml aliquot of 0.01 N $K_2Cr_2O_7$ solution in 250 ml beaker.
- Dilute to 100 ml with distilled water.
- Add 10-15 ml sulphuric acid.
- Titrate against sod. thiosulphate.
- Near an end point add 1 ml starch solution.
- Continue titration till colourless solution obtained (i.e. disappearance of blue colour).

Calculations

$$N.\ Na_2S_2O_3 = \frac{ml\ K_2Cr_2O_7 \times N_{K2Cr2O7}}{ml\ Na_2S_2O_3}$$

Procedure for determination of residual chlorine in water and waste water

- Take suitable aliquot of water/ wastewater in 250 ml beaker.
- Add 5-10 ml acetic acid to make acidic.
- Dilute to about 100 ml with distilled water.
- Add 1-2 gm pot.iodide crystals to liberate iodine.
- Titrate liberated iodine against standard sod.thiosulphate solution.
- Near an end point add 1-2 ml starch solution.
- Continue titration till disappearance of blue colour.
- Carry out blank and deduct from total volume.

Calculations:

$$R.Cl_2,\ mg/L = \frac{ml\ Na_2S_2O_3 \times N\ Na_2S_2O_3 \times 1000 \times 35.45}{ml,\ aliquot}$$

If aliquot = 50 ml, then

$$\boxed{R.Cl_2,\ mg/L = ml\ Na_2S_2O_3 \times N\ Na_2S_2O_3 \times 20 \times 35.45}$$

6.19 ANALYSIS OF CHLORIDES IN WATER, WASTEWATER AND SOIL SAMPLES

Chloride is always found in water and wastewater. The concentration of chloride may be higher in wastewater than raw water because sodium chloride is most essential article of human diet and passes unchanged through a digestive system.

DETERMINATION OF CHLORIDE BY ARGENTOMETRIC METHOD

A. PRINCIPLE

In an almost neutral or in slightly alkaline solution, potassium chromate can indicate the end point against titration of silver nitrate solution (yellowish to dirty orange).

Interference

Substances normally found in potable waters will not interfere. Sulphide, thiosulphate and sulphite ions interfere and can be removed giving treatment with hydrogen peroxide solution. Colour and turbidity also interfere and can be removed using aluminium hydroxide suspension.

Reagents

i. **Standard chloride solution :** Dissolve 0.16486 gm NaCl(AR) in distilled water & dilute to 1000 ml with distilled water (1 ml = 100 μg Cl)
ii. **Standard silver nitrate solution:** Dissolve 1.6987 gm $AgNO_3$ (AR) in distilled water and dilute to 1000 ml distilled water. Store in a brown bottle or wrap a carbon paper to the bottle or volumetric flask.
iii. **Potassium chromate indicator solution:** Dissolve 5 gm (K_2CrO_4) potassium chromate in water and dilute to 100 ml.
iv. **Aluminium hydroxide suspension solution:** Dissolve 125 gm aluminium pot.sulphate or aluminium ammonium sulphate in water. Warm and add 55 ml conc. ammonia solution with stirring. Allow to stand for 1 hour. Decant supernatant. Repeat for 2-3 times to remove chloride ions. Make up to 1000 ml. Use this for removal of interference like colour.
v. **Hydrogen peroxide:** Use 30% H_2O_2 solution.
vi. **Sulphuric acid solution:** 1 N solution to adjust pH.

vii. **Sod. Hydroxide solution:** 1 N solution to adjust pH.

B. PROCEDURE : FOR COLOURLESS AND NO INTERFERING SUBSTANCES

- Take suitable aliquot of solution (water, wastewater) in 250 ml beaker.
- Adjust pH to around 7 to 10, by adding H_2SO_4/NaOH solutions.
- Add 1 ml potassium chromate solution.
- Titrate against 0.1 N $AgNO_3$ (silver nitrate) solution.
- Dirty orange colour shows the end point.

C. PROCEDURE : FOR COLOURED AND INTERFERING SUBSTANCES

a.
  i. Take suitable aliquot of the sample in 250 ml beaker.
  ii. Dilute to about 100 ml with distilld water.
  iii. In case of coloured sample add 3-4 ml aluminium hydroxide suspension, mix thoroughly. Allow to settle and filter.
  iv. Use above filtrate for determination of chlorides.
  v. Add 1 ml potassium chromate solution.
  vi. Titrate against 0.1 N Silver Nitrate ($AgNO_3$) solution.
  vii. Dirty orange colour shows the end point.

b.
  i. In case of sulphide, thiosulphate and sulphite are present in the solution.
  ii. Add 1 ml H_2O_2 solution.
  iii. Stir well for about 2 minutes
  iv. Adjust pH 7-10 by adding H_2SO_4/NaOH solution.
  v. Add 1 ml pot.chromate solution.
  vi. Titrate against 0.1 N silver nitrate solution ($AgNO_3$).
  i. Dirty orange colour shows the end point.

STANDARDIZATION OF SILVER-NITRATE SOLUTION

- Take suitable aliquot of standard sodium chloride solution in 250 ml beaker.
- Dilute to about 100 ml with distilled water.
- Adjust pH 7-10 using H_2SO_4/NaOH solutions.
- Add 1 ml potassium chromate solution.
- Titrate against 0.1 N silver-nitrate solution.
- Dirty orange colour shows the end point.
- Carry out blank in a same manner.

Calculations of standard silver nitrate solution.

$$\text{N AgNO}_3 = \frac{\text{(ml NaCl – ml Blank) x N NaCl}}{\text{ml, AgNO}_3\text{ consumed}}$$

Calculations for determination of chloride concentration

$$\text{Cl, mg/L} = \frac{\text{ml, AgNO}_3\text{ (for aliquot) x N AgNO}_3\text{ x 35.46 x 1000}}{\text{ml, aliquot taken}}$$

If aliquot = 50 ml, then,

$$\boxed{\text{Cl, mg/L = ml AgNO}_3\text{ x N}_{\text{AgNO3}}\text{ x 35.46 x 20}}$$

OR

$$\boxed{\text{Cl, mg/L = Cl, mg (in 50 ml) x 20}}$$

(**Note:** Blank is to carried out every time and must be deducted from the volume obtained for experimental aliquot)

D. PROCEDURE FOR DETERMINATION OF CHLORIDE IN SOIL SAMPLES

- Take 5-10 gms soil in 250 ml beaker.
- Add about 50 ml distilled water.
- Stir occasionally for about 1-2 hours.
- Filter through Whatman No.40 filter paper. Wash 2-3 times with distilled water.
- Take filtrate for determination of chloride.
- Adjust pH 7-10 by adding H_2SO_4/NaOH solutions.
- Add 1 ml potassium chromate solution.
- Titrate against standard silver nitrate solution.
- Dirty orange colour shows the end point.

Calculations

$$\text{\% Cl} = \frac{\text{ml AgNO}_3\text{ x N AgNO}_3\text{ x 0.03546 x 100}}{\text{wt. of sample taken (gms)}}$$

(**Note:** Carry out blank and deduct vol. of $AgNO_3$ required for blank).

6.20 DETERMINATION OF ACIDITY OF WATER & WASTEWATER

Acidity is defined as a capacity of neutralization of alkaline materials and expressed in terms of $CaCO_3$.

Reagents

i. **Sodium Hydroxide Solution : (0.01 N) :** Dissolve 4.0 gm (appr.) NaOH in distilled water and dilute to 1000 ml.
ii. **Sodium Carbonate (Na_2CO_3) AR/GR:** Solid.
iii. **Phenolphthalein Solution:** 0.1% solution in methanol or in distilled water.
iv. **Methyl Orange solution:** 0.1% solution in distilled water.
v. **Sodium Thiosulphate Solution: 0.1 N (appr.)** Dissolve 25 gm $Na_2S_2O_3.5H_2O$ in distilled water and dilute to 1000 ml.

STANDARDIZATION OF SODIUM HYDROXIDE SOLUTION

A. Procedure

- Weigh 0.20 gm Na_2CO_3 in 250 ml beaker.
- Add about 100 ml distilled water to dissolve Na_2CO_3
- Add 2-5 drops of Methyl Orange indicator.
- Titrate against hydrochloric acid.
- Note the reading and calculate the normality of HCl.

$$N_{HCl} = \frac{\text{Weight of } Na_2CO_3 \text{ x (gms) x } 1000}{\text{equi. Wt. of } Na_2CO_3 \text{ x ml HCl\_}} = \frac{\text{Wt. of } Na_2CO_3}{53 \text{ x ml, HCl}}$$

(equivalent wt. of Na_2CO_3 = 53)

B

- Take suitable aliquot of NaOH solution in 250 ml beaker.
- Dilute to about 100 ml with distilled water.
- Add 2-5 drops of phenolphthalein indicator.
- Titrate against above N HCl solution.
- Colourless solution is the end point of the reaction.
- Note the volume of HCl and calculate normality of NaOH solution as follows.

$$N_{NaOH} = \frac{N_{HCl} \text{ x ml, HCl}}{\text{ml, NaOH}}$$

Interferences

Residual chlorine, colour, turbidity, iron, aluminium etc. are the common interferences in analysis of acidity.

Residual chlorine can be removed by addition of calculated amount of sodium thiosulphate solution while others can be avoided by carrying out potentiometric titrations.

Procedure : Determination of Acidity In Water, Waste Water

- Take suitable aliquot of sample in 250 ml beaker.
- Dilute to about 100 ml distilled water.
- Add 2-5 drops of methyl orange indicator.
- Titrate against standard sod.hydroxide solution.
- Note down the reading (ml) of colour change (x ml).
- Add 2-5 drops of phenolphthalein in the same solution.
- Continue titration against same standard NaOH solution.
- Red purple colour shows the end point of reaction.
- Note down the volume of NaOH require.

Calculations :

Acidity is calculated and is expressed in terms of mg/l of calcium carbonate.

$$\text{Acidity as } CaCO_3\text{, mg/l, } = \frac{\text{ml}(NaOH_{M.O.}) + \text{ml }(NaOH_{P}) \text{ x N x 50 x 1000}}{\text{ml. aliquot}}$$

if aliquot = 50 ml, then

$$\text{Acidity as } CaCO_3\text{, Mg/L} = \frac{\text{ml, NaOH (Methyl Orange) + ml NaOH (phenol) x 20 x 50}}{\text{ml, aliquot}}$$

(1 ml 1 N NaOH = 50 mg $CaCO_3$)

6.21 DETERMINATION OF ALKALINITY IN WATER & WASTE WATER

Alkalinity is defined as the capacity of an aquous medium to neutralize acid contents. The alkalinity commonly occurs due to dissolved salts of carbonates, bicarbonates, borates, silicates, phosphates and hydroxyl ions.

Alkalinity is determined as phenolphthalein alkalinity at pH 8.3 and total alkalinity with methyl orange at pH 4.5 by titrating against standard hydrochloric or sulphuric acid.

Interference

Likewise in acidity determination, in alkalinity also there is interference of colour, turbidity, iron aluminium and residual chlorine. Residual chlorine can be removed by addition of calculated amount of sodium thiosulphate solution while colour and turbidity can be avoided by titrating potentiometric method.

Reagents

i. **Standard hydrochloric or sulphuric acid solutions (0.01 N):** Dilute 0.9 ml (appr.) concentration, HCl or 0.3 ml (appr.) conc. H_2SO_4 to 1000 ml with distilled water.

ii. **Solid Na_2CO_3 (AR/GR).**

iii. **Phenolphthalein indicator solution:** Dissolve 0.1 gm in methanol and dilute to 100 ml.

iv. **Methyl Orange indicator solution:** Dissolve 0.1 gm in distilled water dilute to 100 ml.

Standardization of HCl OR H_2SO_4 solutions

Procedure

- Weigh 0.20 gm Na_2CO_3 (AR/GR) in 250 ml beaker.
- Dissolve in water and dilute to about 100 ml with distilled water.
- Add 2-5 drops of methyl orange indicator.
- Titrate against 0.01 N HCl or H_2SO_4.
- Purple colour shows the end point of reaction.

Calculations

$$\text{N HCl OR N } H_2SO_4 = \frac{\text{Weight of } Na_2CO_3 \times 1000}{\text{Equi. Wt. of } Na_2CO_3 \times \text{ml HCl/ml } H_2SO_4}$$

$$= \frac{\text{Wt. of } Na_2CO_3 \times 1000}{53 \times \text{ml, HCl/}H_2SO_4}$$

6.21.1 Procedure for The Determination Of Phenolphthalein Alkalinity

- Take suitable aliquot of the sample in 250 ml beaker.
- Dilute to about 100 ml with distilled water.
- Add 2-5 drops of phenolphthalein indicator soloution.
- Titrate against standard HCl or H_2SO_4 solutions.
- Disappearance of purple colour shows the end point.
- Note the volume of acid required.

Calculations

$$\text{Alkalinity (phenolphthalein)} = \frac{\text{ml (acid)} \times \text{N acid} \times 1000}{\text{ml, aliquot}}$$

OR

$$\text{Alkalinity (phenol) as } CaCO_3, \text{ Mg/l} = \frac{\text{ml (acid)} \times \text{N (acid)} \times 1000 \times 50}{\text{ml, aliquot}}$$

(1 ml 1N HCl/H_2SO_4 = 50 mg Ca CO_3)

6.21.2 PROCEDURE FOR THE DETERMINATION OF TOTAL ALKALINITY

- Take suitable aliquot of sample in 250 ml beaker.
- Dilute to about 100 ml distilled water.
- Add 2-5 drops of phenolphthalein indicator solution.
- Titrate against standard acid solution.
- Disappearance of purple colour shows the end point.
- Add 2-5 drops of methyl orange in the same solution.
- Continue titration till pink colour appears which shows the end point of the reaction.
- Note down the volume of acid required.

Calculations

$$\text{Total Alkalinity} = \frac{\text{ml(acid for phen.)} + \text{ml (acid for methyl orange)} \times \text{N (acid)} \times 1000}{\text{ml. aliquot}}$$

Total Alkalinity, as $CaCO_3$, mg/L

$$= \frac{\text{ml(acid for phen.)} + \text{ml (acid for methyl orange)} \times \text{N(acid)} \times 50{,}000}{\text{ml. aliquot}}$$

Relationship of Alkalinity & Expression of Results

i. Alkalinity of phenolphthalein = P
ii. Total Alkalinity (Methyl Orange) = T

Then the relationship as under:

Sl.No.	Values of P & T	OH	CO_3	HCO_3
01	P = 0	O	O	T
02	P < ½ T	O	2P	T-2P
03	P = ½ T	O	2P	O
04	P > ½ T	2P – T	2(T-P)	O
05	P = T	T	O	O

6.22 DETERMINATION OF HARDNESS IN WATER SAMPLES

Hardness occurs due to soluble ions mostly of calcium and magnesium, which affects the quality of water. Hardness of water is measured as the capacity of water to precipitate soap. It can be defined as a characteristic of calcium and magnesium ions expressed as calcium carbonate ($CaCO_3$) and magnesium carbonate ($MgCO_3$) and is determined by EDTA titrimetirc method.

Few metal ions such as Fe, Al, Mn interfere in this method up to some extent but can be masked by the addition of hydroxylamine hydrochloride and triethanolamine solutions Cu, Ni & Pt can be masked by addition of potassium cyanide (KCN) solution before starting a titration.

Reagent

i. **Buffer solution :** (10 pH) : Dissolve 67.6 gms NH_4Cl in 568 ml ammonium hydroxide solution and dilute to 1000 ml with distilled water.
ii. **Buffer solution :** (12 pH) : Dissolve 200 gms KOH in water and dilute to 1000 ml with distilled water.
iii. **Hydroxylamine Hydrochloride solution :** Dissolve 50 gms in water and dilute to 1000 ml with distilled water.
iv. **Triethanol Amine Solution :** Mix 100 ml triethanolamine in water and dilute to 1000 ml with distilled water.
v. **Potassium Cyanide Solution :** Dissolve 10 gm potassium cyanide (KCN) in water and dilute to 100 ml (Note : Deadly poison).
vi. **Erio-chrome Black-T solution :** Dissolve 0.2 gm E.B.T. in methanol methanol and dilute to 100 ml.
vii. **Pattons & Reader Reagent :** Dissolve 0.2 gm R. & P. reagent in methanol and dilute to 100 ml.
viii. **Standard EDTA Solution :** (0.01 M) : Dissolve 3.723 gm EDTA in water, add 2-5 drops of acetic acid if turbidity appears and dilute to 1000 ml with distilled water.
ix. **Zinc Acetate Solution :** (0.01 M) : Dissolve 0.2195 gm Zinc Acetate (AR/GR) in water and dilute to 100 ml with distilled water.
x. **Buffer Solution :** (5.5 pH) : Dissolve 200 gms ammonium acetate in 30 ml acetic acid and dilute to 1000 ml with water.
xi. **Xylenol Orange Solution :** Dissolve 0.2 gm xylenol orange in 100 ml methanol.

STANDARDIZATION OF EDTA SOLUTION AGAINST ZINC ACETATE SOLUTION

Procedure

- Take 25 ml aliquot of 0.01 M Zinc Acetate Solution in 250 ml beaker.
- Dilute to about 100 ml with distilled water.
- Add 5-10 ml buffer solution (5.5 pH) using measuring cylinder.
- Add 2-5 drops of xylenol orange indicator.
- Titrate against 0.01 M EDTA solution.
- Purple colour shows the end point of the titration.

Calculation of Molarity of EDTA

$$M_{\text{Zn-Ac}} \times 25 = M\ \text{EDTA} \times \text{ml EDTA}$$

$$M_{\text{EDTA}} = \frac{M_{\text{Zn-Ac}} \times 25}{\text{ml EDTA}}$$

A. DETERMINATION OF TOTAL HARDNESS IN WATER SAMPLES

Procedure

- Take suitable aliquot of the water sample in 250 ml beaker.
- Add 5-10 ml hydroxylamine hydrochloride solution.
- Add 5-10 ml triethanol amine solution, mix well.
- Add 5-10 ml. cyanide solution if Cu, Ni, Pt ions suspected.
- Add 15-25 ml buffer (pH-10) solution.
- Mix thoroughly the contents.
- Add 5-10 drops of Eriochrome Black T indicator. (Note: A red wine colour shows a correct pH i.e. 10).
- Dilute the content to about 100-150 ml with distilled water and mix thoroughly.
- Titrate the above content against 0.01 M EDTA solution.
- Greenish-blue colour appears at the end of reaction.

Calculations

$$\text{Total Hardness as } CaCO_3\text{, mg/l} = \frac{\text{ml EDTA} \times M_{\text{EDTA}} \times 1000 \times 100}{\text{ml, aliquot}}$$

$$\text{Hardness (Total), mg, } CaCO_3\text{/L} = 2.497\ \{\text{Ca, Mg/L}\} + 4.118\ \{\text{Mg, mg/L}\}$$

(Note : 1 ml 1 M_{EDTA} = 100 mg $CaCO_3$)

B. DETERMINATION OF CALCIUM HARDNESS

Procedure

- Take suitable aliquot (equal to total hardness aliquot) of sample in 250 ml beaker.
- Add 5-10 ml hydroxylamine hydrochloride solution.
- Add 5-10 ml triethanolamine solution.
- Add 5-10 ml cyanide solution (if Cu, Ni, Pt suspected).
- Add 15-25 ml buffer (pH = 12) i.e. 20% KOH solution.
- Mix thoroughly.

- Add 5-10 drops of Patton & Reader's reagent.
- Dilute the contents to 100-150 ml with distilled water.
- Titrate against 0.01 M EDTA solution.
- Greenish-blue colour shows the end point.

Calculations

$$\text{Calcium hardness as Ca, mg/l} = \frac{\text{ml EDTA X M}_{\text{EDTA}} \text{ x 1000 x 40}}{\text{ml, aliquot}}$$

OR

$$\text{Calcium Hardness as CaCO}_3\text{, mg/L} = \frac{\text{ml EDTA X M}_{\text{EDTA}} \text{ x 1000 x 40 x 2.497}}{\text{ml, aliquot}}$$

C. DETERMINATION OF MAGNESIUM HARDNESS

Calculation

$$\text{Mg-hardness as CaCO}_3 = \frac{\{\text{ml EDTA (Total) – ml EDTA for Ca}\} \text{ x 1000 x 24 x 4.118}}{\text{ml, aliquot.}}$$

6.23 ANALYSIS OF HEXAVALENT CHROMIUM IN DRINKING WATER, WASTE WATER BY COLORIMETRIC METHOD USING 1-5 PHENYLCARBAZIDE

Chromium may exist in water supplies in both hexavalent & trivalent state although trivalent state rarely found in potable water.

Hexavalent chromium is determined colorimetrically by using 1, 5-diphenylcarbazide as a coloring reagent. A red-violet colour is produced can be measured at 540 nm.

Reagents

i. **Chromium stock solution :** Dissolve 0.2828 gm $K_2Cr_2O_7$ in water and dilute to 1000 ml with distilled water. (1 ml = 100 μg Cr.)
ii. **Standard chromium solution :** Dilute 1 ml of 100 μg Cr solution to 100 ml volumetric flask. (1 ml = 1 μg Cr).
iii. **1,5 Diphenylcarbazide solution** : Dissolve 0.50 gm 1,5- diphenylcarbazide in 100 ml acetone.
iv. **Sulphuric acid (0.2N) :** Dilute 5.6 ml conc. H_2SO_4 to 1000 ml.
v. **Potassium permanganate solution :** Dissolve 4 gm $KMnO_4$ in 100 ml distilled water.
vi. **Phosphoric acid :** concentrated and 70% solution.

vii. **Sodium azide solution** : Dissolve 0.5 gm NaN_3 in 100 ml distilled water.

Preparation of Standard graph

- Take a suitable aliquot from standard chromium solution in the range of 2 μg Cr to 10 μg Cr in 100 ml volumetric flask.
- Add 2 ml (70%) phosphoric acid solution, in each volumetric flask mix.
- Add 2 ml diphenylcarbazide solution, mix.
- Make up the volume with 0.2N H_2SO_4, mix thoroughly.
- Allow to stand for 5-10 minutes to develop a colour.
- Take absorbance/transmittance at 540 nm.
- Plot a graph of concentrations against absorbances obtained as above.

Measurement of chromium hexavalent in water and wastewater samples.

A. Procedure in absence of oxidizing or reducing substances

- Filter water, wastewater sample through 0.45 um filter if any suspended solids/particles present in sample.
- Take suitable aliquot of filtered sample in 100 ml volumetric flask.
- Add 2 ml phosphoric acid solution, mix (70%).
- Add 2 ml diphenylcarbazide solution, mix.
- Dilute to 100 ml with 0.2N H_2SO_4 solution, mix thoroughly.
- Allow to stand for 5-10 minutes to develop a colour.
- Take absorbance/transmittance at 540 nm.
- Find out the concentration of chromium from a standard graph.

B. Analysis of Chromium Hexavalent in presence of oxidizing or reducing substances

Reagents

i. **Sodium hypochlorite solution :** Dilute 70 ml sodium hypochlorite solution (NaOCl) to 1000 ml with distilled water.
ii. **Potassium iodide starch test paper.**
iii. **Phosphoric acid solution :** Dilute 700 ml (H_3PO_4) phosphoric acid to 1000 ml with distilled water.
iv. **Sodium chloride :** AR grade NaCl.
v. **1,5-diphenylcarbazide solution : (1%) :** Dissolve 1 gm of 1.5-diphenylcarbazide in acetone and dilute to 100 ml.

Procedure

- Take suitable aliquot of the filtered sample in 100 ml volumetric flask.
- Add 1 ml sodium hypochlorite solution, mix.

- Check the excess of chlorine using potassium iodide starch paper. If there is no excess of chlorine, then add more sodium hypochlorite solution until excess is obtained.
- Add 2 ml phosphoric acid solution, mix.
- Add 10 gm NaCl. Dissolve and mix.
- Pass air through the solution as obtained above at the rate of 40 l/h (appr.) for about 40 minutes (Process may be done in fuming chamber).
- Add 2 ml 1,5-diphenylcarbazide solution, mix thoroughly and dilute to 100 ml.
- Take absorbance after 5-10 minutes at 540 nm.

Procedure : Removal of Molybdenum, Vanadium, Iron & Copper

Reagents

i. **Cupferon solution :** Dissolve 5 gms. cupferon ($C_6H_5N(NO)ONH_4$) in 95 ml water.
ii. **Chloroform** : $CHCl_3$
iii. **Nitric Acid :** Concentrated
iv. **Sulphuric acid.**

- ❖ Take suitable aliquot of sample in 125 ml separating funnel
- ❖ Cool on ice bath.
- ❖ Add 5 ml ice-cold cupferon solution, shake well and keep on ice bath for 1-2 minutes.
- ❖ Add 5 ml $CHCl_3$. Shake vigorously with aquous solution.
- ❖ Stand for separating two phases.
- ❖ Discard $CHCl_3$ layer.
- ❖ Repeat above process of $CHCl_3$ extraction for three times.
- ❖ Take aquous extract in 250 ml conical flask. Wash separating funnel with small amount of distilled water.
- ❖ Boil content for 5 minutes to volatile chloroform, cool.
- ❖ Add 5 ml concentrate HNO_3.
- ❖ Add 3 ml concentrate H_2SO_4.
- ❖ Boil solution upto appearance of SO_3 fumes, cool.
- ❖ Add 5 ml con. HNO_3 again and boil up to all NO_3 fumes evolved (escaped). Cool and use this solution for the determination of chromium hexavalent as described earlier.

C. Oxidation of Trivalent Chromium

Reagents

i. **Sulphuric Acid :** 1:1 H_2SO_4 solution.
ii. **Ammonium solution :** 1:1 Ammonia solution.

iii. **Potassium permanganate solution : (1N)** : Dissolve 3.6 gm $KMnO_4$ in 100 ml volumetric flask and dilute with distilled water.

iv. **Sodium azide solution (0.5%)** : Dissolve 0.5 gm NaN_3 in water and dilute 100 ml with distilled water.

v. **Phosphoric acid solution** : Use con. H_3PO_4.

Procedure

- Take suitable aliquot of sample in 100 ml conical flask.
- See the pH of solution using pH paper.
- Add ammonia solution to make it just alkaline.
- Add dil. H_2SO_4 dropwise just to make it acidic and add 2 ml excess.
- Heat to boiling.
- Add 2 drops $KMnO_4$ solution until red colour persists.
- Boil for 2 minutes.
- Add 1 ml sodium azide solution and boil.
- If red colour does not fade completely after boiling add another 1 ml sodium azide solution and continue boiling till there is no colour.
- Add 5 drops H_3PO_4 solution.
- Transfer the content in 100 ml volumetric flask.
- Adjust pH to 1-1.5 using pH meter or pH paper.
- Add 2 ml diphenylcarbazide solution, mix thoroughly.
- Stand for 5-10 minutes to develop a colour.
- Measure absorbance at 540 nm.

Calculations

$$Cr^{+6}\text{, mg/L} = \frac{\mu g Cr \text{ in aliquot x } 1000}{\text{ml, aliquot}}$$

If aliquot = 50 ml, then,

$$\boxed{Cr^{+6}\text{, mg/L} = \mu g Cr^{+6} \text{ in aliquot x } 20}$$

ANALYSIS OF CHROMIUM HEXAVALENT IN SOLID SAMPLES

Procedure

- Weigh 0.5-1 gm solid sample in silica crucible (-100 mesh)
- Ignite at 550°C to destroy carboneous matter, if any.
- Digest residue in 10 ml H_2SO_4 to dissolve chromium hexavalent for about ½ hour.
- Cool.
- Filter through Whatman No.40 filter paper.
- Take filtrate in 100 ml volumetric flask and make to 100 ml with distilled water.
- Take suitable aliquot from above solution.
- Add 2 ml phosphoric acid, mix.

- Add 2 ml diphenylcarbazide solution, mix thoroughly.
- Make the volume with 0.2 N H_2SO_4 solution, mix again thoroughly.
- Stand for 5-10 minutes to develop a colour.
- Measure absorbance at 540 nm.
- Find out the concentration from standard graph.

Calculations :

$$\%Cr^{+6} = \frac{\mu g Cr^{+6} \text{ (in aliquot)}}{\text{Wt.of sample in gms (in aliquot)} \times 10{,}000}$$

$$\text{OR } \%Cr^{+6} = \frac{Cr^{+6} \text{ (gms) in aliquot} \times 100}{\text{Wt.of sample (gms) in aliquot}}$$

6.24 ANALYSIS OF CYANIDE IN WATER, WASTE WATER AND SOLID WASTES USING ION SELECTIVE ELECTRODE AND COLORIMETRIC METHOD

A. ION SELECTIVE ELECTRODE METHOD

Cyanide as CN can be analysed quantitatively by using Ion Selective Electrode and colorimetric method. To avoid interferences, Ion Selective Method is usually preferred. Cyanide is measured using Cyanide Standard Electrode and Double Junction Reference Electrode immersed in the same solution containing cyanide ions.

The electrical potential of an Ion Selective Electrode is a function of the logarithm of the activity of the ions to be measured. The relationship is given by Nernst Equation.

E(measured) = Eo (constant) $\pm$ S log A_{CN}
Where E = measured electrode potential
Eo = Reference electrode potential (constant)
A = Cyanide ion activity in solution
S = Electrode Slope (constant)
(A) = y x c = concentration
Where y = activity coefficient (constant)

If the activity coefficient is constant then activity is directly proportional to the concentration of cyanide ions present in the solution at pH >12. This can be easily achieved by adding 0.2 M NaOH solution as an Ionic Strength Buffer in a 1:1 ratio of solution and buffer.

Reagents

i. **Standard Cyanide solution :** Dissolve 1.88 gm NaCN (AR) in water and dilute to 1000 ml with distilled water in polythene volumetric flask. (1 ml = 1000 mg/l =1000 PPM CN).

ii. **Ionic Strength Buffer :** (0.2 M NaOH) : Dissolve 8 gm NaOH in water with constant stirring. Cool and dilute to 1000 ml in polythene volumetric flask.

Preparation of Standard Graph

- Take suitable volume of standard stock solution of cyanide and prepare series of 4-5 solutions of 0.2 PPM, 0.4 PPM, 0.6 PPM, 0.8 PPM & 1.0 PPM CN solution in 100 ml volumetric flasks.
- Take aliquot (25 ml) of above solutions in 100 ml polythene beaker.
- Add equal volume (25 ml) 0.2 M NaOH (ionic strength buffer in the same beaker).
- Place one magnetic stirrer bar in the solution.
- Place a beaker containing solution on a magnetic stirrer.
- Immerse cyanide and Reference electrodes in the solution.
- Switch on the main instrument and magnetic stirrer.
- Allow to equilibriate the reaction i.e. to stabilize a reading on the meter.
- Note a reading on the meter.
- Replace first beaker and repeat a process for other solutions of higher concentrations as prepared above.
- Plot a standard graph between concentrations and readings shown by the meter for each concentrations.

Measurement of cyanide concentration in water and wastewater

- Take suitable aliquot of water, wastewater (25 ml or 50 ml) in 100 ml polythene beaker.
- Add equal volume of 0.2 M NaOH buffer (25 ml or 50 ml) in the same beaker
- Place one magnetic stirrer bar in the beaker.
- Place this beaker on the magnetic stirrer.
- Immerse the cyanide and Reference electrode in the solution.
- Switch on the main instrument and magnetic stirrer.
- Allow to equilibrate the reaction i.e. allow to stabilize a reading on the meter.
- After stabilization note down the reading on the meter.
- Find out the concentration of cyanide obtained from the standard graph.

Calculations

$$\text{CN, mg/l} = \frac{\text{mg CN (in aliquot)} \times 1000}{\text{ml, aliquot}}$$

If aliquot = 50 ml then

$$\boxed{\text{CN, mg/l} = \text{mg, CN(in 50 ml)} \times 20}$$

Measurement of cyanide in solid waste

- Take 50 gm of solid waste or more in a polythene beaker of suitable size.
- Add about 50 ml distilled water. Stirrir the content occasionally for about one hour.
- Filter in 100 ml polythene volumetric flask, wash with distilled water.
- Make up the volume to 100 ml with distilled water.
- Take suitable aliquot (25 ml or 50 ml) from above solution.
- Add equal volume of 0.2 M NaOH buffer and measure the concentration of cyanide as mentioned above.

Calculations

$$\text{CN, mg/Kg} = \frac{\text{mg CN(in 1 gm) x 1000}}{\text{Wt. of sample in aliquot (gms)}}$$

$$\text{OR \%CN} = \frac{\text{mg CN (in aliquot) x 100}}{\text{Wt. sample in aliquot (gm) x 1000}}$$

B. ANALYSIS OF CYANIDE BY COLORIMETRIC METHOD

Principle

Cyanide is converted to CN Cl by reaction with chloramines-T at $pH < 8$, which forms a red-blue dye on addition of pyridine-barbituric acid reagent and absorbance can be measure at 578 nm. For better results distillation of samples may be carried out before analysis by above method.

Reagents

i. **Chloramine-T :** Dissolve 1 gm chloramines-T powder in water and dilute to 100 ml.

ii. **Standard solution of cyanide :** Dissolve 1.88 gm NaCN (AR) in water and dilute to 1000 ml in polythene volumetric flask with distilled water. (1 ml = 1000 mg/l = 1000 PPM CN) OR Dissolve 0.1880 gm NaCN(AR) in water and dilute to 1000 ml. (1 ml = 100 PPMCN).

iii. Dilute above 1000 PPM CN solution so that 1 ml = 1 µg CN.

iv. **Pyridine barbituric acid solution :** Dissolve 6 gm barbituric acid in minimum quantity of water. Add to this 30 ml pyridine and 6 ml concentrate HCl. Mix thoroughly, cool and dilute to 100 ml in polythene volumetric flask.

v. **Sodium dihydrogen phosphate (1M):** Dissolve 138 gms NaH_2PO_4 in water and dilute to 1000 ml in polythene volumetric flask.

vi. **Sodium Hydroxide solution :** Dissolve 1.6 gm NaOH in water, cool and dilute to 1000 ml in polythene volumetric flask.

Procedure

Prepration of standard graph :

- Take appropriate volume of the standard stock solution to prepare series of standards ranging from 2 μg CN to 10 μg CN in 100 ml polythene volumetric flask.
- Add 4 ml sodium dihydrogen phosphate buffer in each flask. Mix.
- Add 2 ml chloramines-T solution, mix again.
- Add 5 ml pyridine-barbituric acid solution. Mix thoroughly and dilute to 100 ml with distilled water. Mix thoroughly again.
- Measure the transmittances/absorbance at 578 nm using spectrophotometer of 1 cm cell path.
- Plot a graph between concentrations of cyanide and absorbance obtained.

Measurements of cyanide in samples

- Take suitable aliquot of sample in 100 ml polythene volumetric flask.
- Add 4 ml phosphate buffer, mix.
- Add 2 ml chloramines-T solution, mix again.
- Add 5 ml pyridine-barbituric acid solution, mix thoroughly.
- Make up the volume to 100 ml with distilled water. Mix thoroughly.
- Take absorbance at 578 nm using spectrophotometer. Calculate CN concentration from the standard graph.

Calculations

$$\text{CN, mg/l} = \frac{\text{mg CN(in aliquot)} \times 1000}{\text{ml, aliquot}}$$

If aliquot = 50 ml, then

$$\boxed{\text{CN, mg/l} = \text{mg CN(in 50 ml)} \times 20}$$

6.25 ANALYSIS OF FLUORIDES IN WATER, WASTE WATER, MINERALS, ORES AND SOIL SAMPLES USING ION-SELECTIVE ELECTRODE AND COLORIMETRIC METHOD

A. ION SELECTIVE ELECTRODE METHOD

Whenever a sensing element is in contact with a solution containing fluoride ions, an electrode potential develops across the sensing element. This potential, which depends on the concentration of free fluoride ions in solution is measured against a constant Reference potential with a digital pH/mv meter or specific ion meter.

According to Nernst equation:

$$E = E_o + S \log (A)$$

Where E = measured electrode potential
E_o = Reference electrode potential (constant)
A = fluoride ion activity in solution
S = electrode slope (about 57 mv/decade)

(A) = y x c = ionic concentration
Where y = activity coefficient (constant).

If the activity coefficient is constant then activity is directly proportional to the concentration of ions present in an ionic high strength of background solution.

Total Ionic Strength Adjustor Buffer (TISAB) is added to all fluoride standards and samples so that the background ionic strength should be high.

Reagents

1.

a. **Standard Fluoride Solution :** Dissolve 0.221 gm NaF (AR/GR) in water and dilute to 1000 ml with distilled water in a polythene volumetric flask. (1 ml = 100 PPM F).

b. Dilute 1 ml of 100 PPM F solution to 100 ml in polythene volumetric flask with distilled water. (1 ml =1 PPM F).

2.

i. **Total Ionic Adjustor Buffer (TISAB)** : Dissolve 58 gms NaCl in 57 ml glacial acetic acid.

ii. Add 0.2 gm CDTA (1, 2-diamino cyclohexane N, N, N, N-tetra acetic acid) in TISAB solution.

iii. Mix the contents thoroughly.

iv. Add 125 ml 6N NaOH in TISAB solution, mix again.

v. Make up the volume to 1000 ml.

vi. Check the pH of this TISAB solution. It should be around 5.3-5.5 (otherwise adjust it).

Interferences

Fluoride forms complexes with several polyvalent cations such as Al & Fe. The extent of complexation takes place depends on solution pH, concentration of fluoride and complexing species. CDTA (cyclohexylene diamine tetra acetic acid) a component of buffer, will complexed interfering cations and release free fluoride ions, hence at the pH maintained by buffer, no interference occur.

Procedure for analysis of fluoride in water, waste water samples

A. Standardization of instrument

- Take aliquot of 1 PPM, 2 PPM, 3 PPM, and 4 PPM standard solution of fluoride in 100 ml polythene volumetric flask.
- Make up to 100 ml with distilled water. Mix thoroughly.
- Take suitable aliquot (25 ml) of each standard solution in 100 ml polythene beaker.
- Add equal volume of TISAB buffer in each of the standards.
- Immerse standard and Reference electrodes in to the standard solution.
- Place a beaker on magnetic stirrer.
- Place a stirring bar in the beaker.
- Switch on the main instrument and magnetic stirrer.
- Allow to equillibriate the contents in the beaker and take the measurement of concentrations of standard calibration graph.

(Note: Today most of ISE are having the facilities to calibrate in the instrument itself. If the facilities are not in the instrument graph may be drawn on graph paper).

B. Measurement of Fluoride in water, waste water

- Take suitable aliquot of water, waste water sample in 100 ml polythene beaker.
- Add equal volume of TISAB solution in the beaker.
- Place a stirring bar in beaker.
- Place beaker on the magnetic stirrer.
- Immerse a standard and Reference electrode in the solution.
- Switch on the instrument and magnetic stirrer.
- Allow to stabilize/equillibrate the solution.
- Take reading at constant point (steady state).
- Find out the concentration from the standard graph.

Calculations

$$\text{F, mg/l} = \frac{\text{mg F (in aliquot)} \times 1000}{\text{ml, sample taken}}$$

If aliquot = 50 ml, then

$$\boxed{\text{F, mg/l} = \text{mg F(in 50 ml)} \times 20}$$

ANALYSIS OF FLUORIDE IN MINERALS, ORES, ORE DRESSING PRODUCTS AND SOIL SAMPLES

Procedure

- Fuse 0.1 gm (-100 mesh) (for rich fluoride) or 1 gm sample (for low fluoride) in platinum crucible.
- Add about 5 gm sodium carbonate.
- Place the crucible in Muffle Furnace.
- Fuse the content at 900^{o}C for about 10-15 minutes.
- Take out a crucible and allow to cool at room temperature.
- Extract fused mass in 250 ml Teflon beaker with addition of minimum quantity of hydrochloric acid.
- Make up the volume in 100 ml polythene volumetric flask.
- Take 1 ml of above solution (in case of rich fluoride content) in 100 ml polythene volumetric flask and dilute to the mark OR Take 10 ml aliquot (in case of low fluoride content) and dilute to 100 ml in polythene volumetric flask.

Measurements

- Take suitable aliquot of above solution in 100 ml polythene beaker (i.e. 25 ml aliquot).
- Add equal volume of TISAB buffer.
- Place one bar of magnet in a beaker.
- Place beaker on magnetic stirrer.
- Switch on instrument and magnetic stirrer.
- Immerse fluoride and Reference electrode in the solution.
- Allow to equillibriate the reaction and stabilize the reading on a meter.

Calculations

$$\% F = \frac{\text{Reading (ppm) x dilution factor x 100}}{\text{Wt. of sample (gms) x 10,000}}$$

B. ANALYSIS OF FLUIORIDE BY COLORIMETRIC METHOD : SPADNS METHOD

The SPADNS method is useful for the determination of fluoride in a range of 0 to 1.4 mg F/L, which gives instantaneous colour with zirconic oxychloride forming a zirconium dye lake in acidic condition. Fluoride reacts with above dye lake, dissociating a portion of it into a colourless complex. Hence as the amount of fluoride increases, the colour intensity of the complex decreases. This intensity obeys Beer’s Law in a reverse manner.

Reagents :

a. **Standard Fluoride Solution :** Dissolve 0.221 gm NaF in water and dilute to 1000 ml. (1 ml = 100 ppm F).

b. **SPADNS Solution** : Dissolve 0.1916 gm SPADNS reagent {2-(parasulphophenylazo)-1, 8-dihydroxy –3, 6-naphthalene disulphonate) in water and dilute to 100 ml with distilled. Water

c. **Zirconyl-acid reagent** : Dissolve 0.133 gm Zirconyl oxy-chloride octahydrate ($ZrOCl_2.8H_2O$) in distilled water. Add 350 ml conc. HCl and dilute to 500 ml with distilled water.

d. **SPADNS-Acid Zirconyl Solution** : Mix equal volume of SPADNS solution and zirconyl acid reagent.

e. **Reference Solution** : 10 ml SPADNS reagent solution prepared earliest is diluted to 100 ml. Then 7 ml conc. HCl is diluted to 10 ml. Now add this solution to diluted spadns solution. Mix the solution thoroughly. Use this for setting a zero of the spectrophotometer to be used for the measurement of colour intensity.

f. **Arsenite solution** : Dissolve 0.5 gm Sod. Arsenite ($NaAsO_3$) and dilute to 100 ml with distilled water.

Procedure

Preparation of standard graph

- Take suitable aliquot from the stock solution of fluoride in 100 ml polythene flasks in the range of 0.2 PPM to 1.4 PPM F (i.e. 0.2 PPM, 0.4 PPM, 0.6 PPM, 0.8 PPM, 1 PPM, 1.2 PPM and 1.4 PPM F).
- Add 10 ml mixed acid zirconyl spadns reagent in each of the volumetric flask. Make up the volume with distilled water and mix thoroughly.
- Measure the absorbance/transmissions at 570 nm of each solution.
- Plot a graph, concentrations against absorbance/transmittances.

Measurement of fluoride in water, wastewater samples

- Confirm the presence of residual chlorine. If sample contains residual chlorine, it can be removed by adding 1drop (0.05 ml) $NaAsO_2$ solution which is equivalent to 0.1 mg $R.Cl_2$. Avoid to add excess of $NaAsO_2$ solution.
- Take suitable aliquot of sample in 100 ml polythene volumetric flask (i.e. 50 ml).
- Add 10 ml mixed acid zirconyl-SPADNS reagent.
- Make up the volume with distilled water and mix thoroughly.
- Take absorbance/transmittance at 570 nm.
- Find out the Fluoride concentration from the standard graph.

Calculations:

$$F, mg/L = \frac{mg.F \text{ (from graph in aliquot) x } 1000}{ml.aliquot}$$

If aliquot = 50 ml , then

$$\boxed{F, mg/L = mg.F \text{ (in 50 ml) x } 20}$$

6.26 ANALYSIS OF MERCURY IN WATER/WASTE WATER, MINERALS, ORES AND SOIL SAMPLES USING MERCURY ANALYSER

Mercury is the only element, which occurs in liquid form at room temperature. It is toxic and hence we have to be very much careful about its presence in drinking water. Mercury can be analysed at the trace level using mercury analyzer.

The technique of mercury analysis is known as cold vapour atomic absorption spectrophotometry. It is based on the principle that mercury vapour (atoms) absorbs resonance radiations at 253.7 nm at room temperature.

An instrument consists of

1. Low pressure mercury lamp emitting 253.7 nm resonance line.
2. An absorption cell.
3. A filter
4. Vapour generation system and
5. A detector with associated electronic devices.

The carrier air is bubbled through the vapour generation system, which carries elemental mercury from the solution and then passes through an absorption cell. This can be measured on either optical density meter or on transmission meter.

Preparation of Standard Graph

Reagents

a.

i. **Pot.permanganate solution (1%)** : Dissolve 1 gm $KMnO_4$ in distilled water.

ii. Add 10 ml conc. H_2SO_4 and dilute to 100 ml.

b.

i. **Sodium Hydroxide solution : (20%)** : Dissolve 20 gm NaOH in distilled water

ii. Dilute to 100 ml with distilled water.

c.

i. **Stannous chloride solution : (20% in 10% HCl)** : Dissolve 20 gm $SnCl_2$ (AR/GR) in 10 ml conc. HCl with warming.
ii. Cool and dilute to 100 ml with distilled water.

d. **Sulphuric acid solution** : Prepare 1:1 dilution.

e. **Nitric Acid Solution :** Prepare 10% HNO_3 solution. (i.e. 10 ml conc. HNO_3 is diluted to 100 ml with distilled water).

f.

i. **Standard Mercury Solution** : Dissolve 0.1354 gm $HgCl_2$ in 2% HNO_3.
ii. Dilute to 1000 ml with 2% HNO_3 solution (1 ml = 0.10 mg Hg = 100 μg Hg).
iii. Dilute 10 ml of 100 ug Hg solution to 100 ml with 2% HNO_3 solution.
(1 ml = 10 μg Hg = 10,000 ng Hg).
iv. Dilute 10 ml of 10 ug Hg solution to 100 ml with 2% HNO_3 solution.
(1 ml = 1 μg Hg = 1000 ng Hg).
v. Dilute 10 ml of 1000 ng Hg to 100 ml with 2% HNO_3 solution.
(1 ml = 0.1 μg Hg = 100 ng Hg).

(**Note**: Stock solution of Hg is to be maintained with 2% HNO_3 and 0.01% $K_2Cr_2O_7$ solution).

Standard Graph using BOD Bottle

- Take aliquots of 1 ml, 2 ml, 3 ml, 4 ml, 5 ml & 6 ml from 100 ng Hg stock solution in BOD bottles. (This each solution contains 100, 200, 300, 400, 500 & 600 ng Hg).
- Add required volume of distilled water to maintain the total volume = 100 ml. (Before adding any reagents in BOD bottles).
- Add 5 ml of 10% HNO_3 acid solution in BOD bottle.
- Add 2 ml $SnCl_2$ solution and stopped the BOD bottle immediately. (Up to this stage the total volume in BOD bottle should be 100 ml.).
- Keep this BOD bottle (Mercury vapour generator) on magnetic stirrer and continue for 5 minutes.
- Keep a filter rod on open position and mode switch to ‘Hold’ position.
- Adjust absorbance 0 to 2 by moving adjacent switches or transmission between 0 to 100 by moving adjustment switches of the instrument, as per manufacturer’s instructions.
- After 5 minutes, start the pump and allow mercury vapours to purge through the BOD bottle (i.e. vapour generation bottle).
- Note an absorbance/transmittances on a meter at ‘Hold’ position.
- Plot a standard graph between concentration of Hg and absorbance/transmittances.

DETERMINATION OF MERCURY IN WATER/WASTEWATER/EFFLUENT ETC.

Procedure

- Take suitable aliquot of sample in BOD bottle (for example, 50 ml)
- Take distilled water so that the total volume including other reagents should not be more than 100 ml.
- Add 5 ml of 10% HNO_3 acid solution in BOD bottle.
- Add 2 ml $SnCl_2$ solution and stopper BOD bottle immediately (upto this stage the total volume of BOD content should be 100 ml.)
- Keep BOD bottle as prepared above on magnetic stirrer.
- Start the magnetic stirrer and continue for five minutes.
- Take absorbance/transmittance after 5 minutes.
- Carry out blank in a similar manner and deduct from sample reading.
- Find out the concentration of mercury from the standard graph.

Calculations :

$$\text{Hg, mg/L} = \frac{\text{Hg, ng (in aliquot)} \times 1000}{\text{ml, (aliquot)} \times 1000 \times 1000} = \frac{\text{Hg, ng (in aliquot)}}{\text{ml, aliquot} \times 1000}$$

If aliquot = 50 ml, then

$$\boxed{\text{Hg, mg/L} = \frac{\text{Hg, ng (in 50 ml)} \times 20}{1000}}$$

(**Note** : At the end of every reading, allow mercury vapour to absorb in $KMnO_4$ solution by continuing pump up to a condition that meter shows zero reading).

ANALYSIS OF MERCURY IN MINERALS/ORES AND SAND SAMPLES

Procedure: Preparation Of Solution/Dissolution Of Mercury

- Weigh 1.0 gm finely powdered sample (-100 mesh) in 250 ml beaker.
- Add 10 ml acid mixture (1:1 HNO_3 : H_2SO_4) in the above beaker and cover with watch glass.
- Keep beaker on water bath at about 60^oC and allow to digest for two hours with swirling occasionally.
- Remove beaker from the water bath and allow to cool at room temperature.
- Dilute the content with 20-25 ml distilled water. Allow to cool again.
- Add 5 ml of 6% $KMnO_4$ solution and leave for over night.
- Next day, add 5% hydroxylamine hydrochloride solution dropwise until all brown manganese dioxide and excess of permanganate are reduced. (Almost colourless solution appears).

- Allow the reaction complete for keeping about one hour. During this period all gases are escaped.
- Filter if some turbidity or residue is noticed in the solution.
- Make up a volume to 100 ml in volumetric flask.
- Take suitable aliquot from this solution for the determination of mercury.

ANALYSIS OF MERCURY

- Take suitable aliquot from above solution in B.O.D. bottle (Mercury vapour generation system).
- Add required volume of distilled water to maintain total volume to 100 ml.
- Add 5 ml of 10% HNO_3 solution.
- Add 2 ml of $SnCl_2$ solution (20% in 10% HCl).
- Immediately close the system and keep on a magnetic stirrer with magnetic bids and allow to continue for 5 minutes and take the measurement as described in earlier procedure.
- Run blank in a similar manner and deduct from main reading

Reaction : $\mathbf{HgCl_2 + SnCl_2 \quad = \quad Hg + SnCl_4}$

At room temperature vapour of mercury is generated, which can be measured on optical density/transmission meter.

Calculations

$$\% \text{ Hg} = \frac{\text{(A-B) ng, Hg x 1000}}{\text{Wt. of sample in aliquot (gms) x 1000 x 1000 x 1000}}$$

$$\%\text{Hg} = \frac{\text{(A-B) ng, Hg}}{\text{Wt. of sample in gm x } 10^{7}} = \frac{\text{(A-B) ng Hg x } 10^{-7}}{\text{Wt. of sample in gm}}$$

Where A = concentration of Hg in ng for sample.
B = concentration of Hg in ng for blank.

NON-SPECIFIC ABSORPTION

Vapour of organic compounds such as alcohols, ketones and ester, acids and water vapour will absorb UV radiation and hence will interfere seriously, as absorption of UV (ultraviolet) radiation by mercury atoms occurs in this technique. All substances, which absorbs UV radiation will decrease the transmittance and cause positive bias. The absorption due to these substances is knows as ‘Non-specific’ absorption.

DETERMINATION OF NON-SPECIFIC ABSORPTION

The traps of alkali and acid will remove acid and water vapour respectively and therefore will minimize non-specific absorption. However, if non-specific absorption is suspected in unknown sample, it can be measured by adopting the following procedure.

- Remove the trap of H_2SO_4 (R_4)
- Place another trap containing 4 ml of 1% $KMnO_4$ solution (1:1 H_2SO_4 solution) say it as R_6.
- Now repeat the analysis on a separate aliquot of sample as usual manner.
- Note the absorbance obtained, which is of non-specific absorbance and not due to mercury as R_6 absorb all mercury vapour before going to absorption cell.
- The difference of two absorbances will give absorbance due to that of mercury alone.

Calculations

$$AHg = AR_4 - AR_6$$

Where
AHg = absorbance due to Hg alone
AR_4 = absorbance due to Hg + other organic materials
AR_6 = absorbance due to other organic materials.

$$\boxed{A_{R6} = A_{R4} - A_{Hg} = \text{Non-specific absorbance}}$$

6.27 SOIL ANALYSIS

Soil is the upper layer of earth crust. Most of the plants growth depends upon the type of soil from which they take water and nutrients. The quality of soil is decided by taking some factors into considerations and is to be determined using appropriate methods of analysis such as physical and chemical properties on which the fertility of soil can be decided. Due to some man made activities the soil has been disturbed and needs to take proper care to achieve the effectiveness of its origin.

Some important soil parameters can be analysed using the following procedures.

A. Physical parameters

- Particle size analysis
- Water holding capacity

B. Chemical parameters

- pH
- Soluble salts

- Organic carbon
- Cation exchange capacity
- Calcium carbonate
- Available phosphorous
- Available sulphur &
- Nitrogen, etc.

Soil testing involves the following steps

1. Sampling of soil to be tested
2. Analysis of various physical and chemical parameters.

SAMPLING

The principal object of this step is to collect the representative samples of the entire area. Some criteria is to be followed while collecting soil samples such as an area can be considered as a single sampling unit only if it is appreciably uniform in all respects. The spots located near bunds, channels, marshy tracts and spots near trees, wells, compost piles or any other location that can be considered non-representative of the general area should be avoided.

Sampling depth is another important aspect. It is usually advised to take sample at the depth of 15 cms from the surface of top soil, which can be extended up to 22 cms in some cases.

Keeping the above points in mind, the following steps must be followed while collecting the soil samples.

1. First of all, visually inspect the area to be sampled. If considerable differences in colour, texture, elevation etc. are existing, divide entire area into sampling units or if there are no considerable differences noticed then the whole area can be treated as a single sampling unit.
2. Take as many as possible 10-20 samples from spots distributed covering the entire area. At each spot scrap away any surface little and collect in a clean cloth or plastic bags using appropriate instrument and collect enough quantity as per requirements for the testing purposes.

Collected samples are to be air dried and crush into desired size, either by hammering or using any mechanical instrument. Crushed samples are then subjected to coning and quartering process so that a representative sample can be obtained from the original sample.

Thus the sample obtained as above should properly labeled and preserved from being contaminating with other materials such as chemicals, fertilizers, etc.

If possible sample may be divided into two separate portions so that one can be used for physical tests, while other can be crushed into fine powder and used for the analysis of chemical parameters.

The samples must be analysed as early as possible since some parameters having the tendency to change with passing of time.

ANALYTICAL PROCEDURES : PHYSICAL PARAMETERS

DETERMINATION OF SOIL TEXTURE : GRAVIMETRIC METHOD

The objective of textural analysis of soil is to determine the percentage of solid material contained in different size fractions. This can be done either gravimetric or mechanical method.

Reagents

1. **Hydrogen peroxide :** 20 ml (30%) hydrogen peroxide is diluted to 100 ml with distilled water.
2. **Hydrochloric acid : (2N)** : 83 ml conc. HCl is diluted to 500 ml with distilled water.
3. **Sodium Hydroxide Solution : (2N) :** Dissolve 40 gms NaOH in water and dilute to 500 ml with distilled water.
4. **Silver Nitrate Solution (1%) :** Dissolve 1 gm $AgNO_3$ in water and dilute to 100 ml with distilled water.

Procedure

- Take 10 gm of –2 mm soil sample in 500 ml beaker.
- Add 125 ml distilled water, boil for about 10 minutes.
- Allow to cool and to settle suspension.
- Decant supernatant and discard it.
- Add 20 ml H_2O_2 solution and digest on water bath adding more H_2O_2 Solution till no froathing is evolved.
- Add about 20-30 ml 2N HCl and dilute to about 100 ml distilled water.
- Allow to stand about one hour with occasional stirring to make the soil free from carbonates.
- Filter through Whatman No.41 filter paper. Wash residue with distilled water till free from chloride ions. (Test with $AgNO_3$ solution).
- Transfer residue of soil in beaker.
- Add 5 ml, 2N NaOH solution and shake for about ½ an hour.
- Transfer the content in 1000 ml measuring cylinder and make up the volume to 1000 ml with distilled water.
- Shake the above contents thoroughly for about 1 minute, and allow to stand.
- Take 25 ml volume with pipette at 10 cm depth after 4 minutes in preweighed platinum dish or in preweighed beaker.

- Evaporate at 105°C in oven and weigh to constant weight.
- The difference in weight is contributed by clay+silt.
- Shake remaining content in the measuring cylinder for about 1 minute and keep for settlement.
- Take 25 ml volume with pipette at 10 cm depth in preweighed platinum crucible/dish or in beaker after 6 hours.
- Evaporate at 105°C in an oven and find out the weight after it is dried completely.
- Weight difference gives the weight of clay alone.

Calculations

1. Calculate % of clay alone obtained.
2. Calculate % of clay + silt as obtained above.
3. Substract weight of clay from weight of clay+silt, which gives only silt %.
4. Substract weight of clay + silt from 100%, which gives sand percentage. i.e. Sand % = 100 – (% clay + % silt).

Let wt. of sample = W_0 gms.
Of clay alone = W_1 gms
Wt. of clay + slit = W_2 gms
Aliquot = 25 ml
Total volume = 1000 ml.

$$\text{Then \% of clay} = \frac{(W_1)\text{ gm x Total Volume x } 100}{\text{Wt. of soil sample x ml. aliquot}}$$

$$= \frac{(W_1) \times 1000 \times 100}{W_0 \times 25} = \frac{(W1) \times 4000}{W_0}$$

$$\text{\% Slit} = \frac{(W_2 - W_1) \times 4000}{W_0}$$

$$\text{\% Sand} = 100 - \left[\frac{(W_1) \times 4000}{W_0} + \frac{(W_2 - W_1) \times 4000}{W_0} \right]$$

(Note: If soil containing MnO_2, add few drops of acetic acid before treatment of H_2O_2.
In case of calcareous soil, use H_2O_2 slightly acidified with HCl.
The pulp density of suspension should not be more than 2% to have a good result

SOIL TEXTURE (MECHANICAL METHOD)

Different methods are used for the determination of sand (coarser than 0.062 mm) and silt + clay (finer than 0.062mm). Samples are dried and sieved on series of sieves starting from highest diameter at the top and finest at the bottom. The method of analysis of particle size distribution of sediments/soils depends on whether sediment/soil is relatively coarse or fine.

The soil/sediment samples are sieved through different pore sizes for separating different fractions of soil/sediment.

Procedure

- Dry soil/sediment samples at 105°C in an oven.
- Take 100-500 gms of soil/sediment sample in a tray.
- Arrange sieves of 2 mm (at the top), 1 mm, 500 mesh, 250 mesh, 125 mesh and 63 mesh with decreasing aperture size .
- Place the weighed sample on the top of the sieve shaker.
- Start the sieve shaker and allow to run for 10-15 minutes.
- Collect sample from each sieve.
- Take weight of each fraction of collected sample.
- +2 mm may be weighed and calculate percentage which is called granules.

Calculations

The distribution of particle size of sample can be represented as below

Sl.No.	Size of Particle	Grain Name
1.	+2 mm	Granules
2.	-2 mm+500 mesh	Very coarse sand
3.	-500+250 mesh	Coarse sand
4.	-250+125 mesh	Medium sand
5.	-125+63 mesh	Fine sand
6.	-63 mesh	Silt and clay

$$\% \text{ of each fraction of soil} = \frac{\text{Wt. of each fraction x 100}}{\text{Wt. of sample taken}}$$

B. CHEMICAL PROPERTIES

DETERMINATION OF pH

The measurement of hydrogen ions (or hydroxyl ions) activity of soil-water system is known as soil pH. This indicates the nature of soil reaction.

Procedure

- Take 10 gm of soil sample in 100 ml beaker.
- Add 50 ml distilled water.
- Mix and occasionally stir for about 30 minutes.
- Measure pH of above suspension using standard pH meter

(Note : pH meter can be standardized using standard pH solutions of 4.0, 7.0 & 9.2).

DETERMINATION OF ELECTRICAL CONDUCTIVITY

Conductivity is a measurement of current carrying capacity, which gives idea about the soluble salts present in soil samples.

Procedure

- Take 10 gms soil sample in 100 ml beaker.
- Add 50 ml distilled water.
- Stir for about 1 hour with intervals.
- Measure the conductivity of above suspension using standardized conductivity meter.
- Conductivity meter can be standardized using KCl (AR) of suitable concentration.

Calculations

Conductivity (us/cm OR mhos/cm) = Cell constant x meter reading

(Or as per the instructions of instrument manufacturer).

DETERMINATION OF WATER HOLDING CAPACITY OF SOIL SAMPLES

Water holding capacity of soil depends upon the physical and chemical nature of it. When the soil is absolutely saturated with water so that water fills all the pores between particles of soil and there is no air space, the soil is said to be at its maximum Water Holding Capacity.

Procedure

- Dry sample in oven at 105°C
- Place a filter paper (Whatman No.1) in a rectangular perforated box at the bottom.
- Take weight of box.
- Fill perforated box with soil to be tested.
- Take weight of box with filled soil.
- Place above box in petri dish/tray or suitable pot.
- Fill water in petri dish/tray just below the edges of perforated box.
- Allow to stand for 12 hours to saturate the soil by entering water through holes.
- Take out box after 12 hours.
- Dry box on outside using tissue paper.
- Take weight of the box with saturated soil.

Calculations

$$\text{W.H.C. \%} = \frac{(W_2 - W_1) - (W_1 - W_0) \times 100}{(W_1 - W_0)}$$

$$= \frac{(\text{Wt. of water saturated soil}) - (\text{Wt. of dried soil}) \times 100}{\text{Wt. of dried soil}}$$

Where W_0 = Wt. of empty box
W_1 = Wt. of box with dried soil
W_2 = Wt. of box with water saturated soil

DETERMINATION OF ORGANIC CARBON

For the determination of organic carbon (matter) in soil samples, sample digested with excess of potassium dichromate solution in presence of sulphuric acid and excess of dichromate is determined by titrating against ferrous ammonium sulphate solution.

Reagents

1. **Potassium dichromate solution (1N)** : Dissolve 49 gms $K_2Cr_2O_7$ in distilled water and dilute to 1000 ml with distilled water.
2. **Sulphuric acid with silver sulphate : (5%)** : Dissolve 5 gm silver sulphate (Ag_2SO_4) in 100 ml conc. H_2SO_4.
3. **Phosphoric acid** : 85%
4. **Ferrous Ammonium Sulphate Solution (1N**) : Dissolve 392.2 gm Ferrous Ammonium Slulphate $\{Fe(NH_4)_2\ (SO_4),\ 6H_2O\}$ in 20 ml conc. H_2SO_4 and dilute to 1000 ml with distilled water.
5. **Barium diphenylamine sulphonate indicator** : 0.5% : Dissolve 0.5 gm Barium diphenylamine sulphonate in water and dilute to 100 ml. with water.

Procedure

- Take 0.5-1.0 gm soil sample in 500 ml conical flask. Moisten with few ml of distilled water.
- Add 10 ml potassium dichromate (1N) solution using pipette.
- Add 20 ml sulphuric acid – silver sulphate mixture solution.
- Mix gently and allow to stand for ½ an hour.
- Dilute mixture to about 200 ml with distilled water.
- Add 10 ml phosphoric acid, mix thoroughly. Cool.
- Add 1 ml Barium diphenylamine sulphonate indicator.
- Titrate above solution with 1 N Ferrous Ammonium sulphate solution.
- Brilliant green colour shows the end point of the reaction.
- Carry out the blank in a similar manner.

Calculations

$$\text{Organic Carbon \%} = \frac{\text{ml (Blank)} - \text{ml (Sample)}\ N_{FAS} \times 0.003 \times 100}{\text{Wt. of sample}}$$

$$= \frac{\text{ml (Blank)} - \text{ml (Sample)} \times N_{FAS} \times 0.3}{\text{Wt. of sample}}$$

$$\text{Organic Matter} = \%\ C \times 1.724$$

(Note: The factor 1.724 is based on the assumption that carbon is only 58% of organic matter)

(1 ml 1 N $K_2CR_2O_7$= 0.003 gm Organic Carbon = 1N FAS)

DETERMINATION OF CATION EXCHANGE CAPACITY

For the determination of cation Exchange Capacity 1 N.Sodium acetate solution of pH 8.2 is used. In this technique, sodium replaces all the exchangeable cations of soil when leached thoroughly and excess sodium ions are removed using ethyl alcohol. These sodium ions can be easily determined using flame photometer.

Reagents

1. **Sodium acetate solution : (1N, pH = 8.2) :** Dissolve 40.0 gm sod. hydroxide in distilled water. Add 58 ml acetic acid and dilute to 1000 ml with distilled water. Adjust pH = 8.2 using NaOH.
2. **Ethyl alcohol :** 95%
3. **Ammonium acetate** : (1N, pH = 7.0) **:** Mix 58 ml acetic acid and 68 ml conc. ammonium hydroxide solution and dilute to 1000 ml. Adjust pH to 7.0 using NH_4OH or Acetic Acid.

Procedure

A.

- Take 5 gms of soil (powder) in 50 ml centrifuge tube.
- Add 30 ml 1 N sodium acetate solution.
- Stopper and shake for 5 minutes.
- Centrifuge the suspension. Till supernatant is clear.
- Decant the supernatent and discard
- Repeat above process for three times using 30 ml sodium acetate solution every time.

B.

- Sodium saturated sample is then washed thrice with 30 ml of 95% ethyl alcohol with shaking 5 minutes each time.
- Wash with 20 ml ethyl alcohol till the supernatent shows conductivity between 55-40 us/cm.

C.

- The absorbed sodium is replaced from the sample with 30 ml volume of 1 N. Ammonium acetate solution.
- Repeat for thrice.
- Decant the supernatent in 100 ml volumetric flask.
- Make upto the mark with ammonium acetate solution.
- Determine sodium using Flame Photometer.
- Carry out a blank in a similar manner.

Calculations :

$$\text{Cation Exchange Capacity (meq/100 gms)} = \frac{\text{A x V ml x 100 x 100 ml}}{\text{W x 23 x 1000 ml}}$$

$$= \frac{\text{A x Vml x 10}}{\text{23 x Wt. of soil sample}}$$

Where A = Na content in ammonium acetate extract (meg/L)
V = ml volume of extract, ml
W = Wt. of soil sample taken in grams.

(1 meq/100 gm = 1 mg. Eq./100 gm For sod. Na = 23)
(1 meq/L of Na = 0.023 gms of Na)

(**Note:** $\text{ppm} = \frac{\text{Atomic mass of atom x meq}}{\text{Valency of atom}}$

(i.e. 1 meq of Na = 23 ppm = 0.023 gms Na)

DETERMINATION OF EXCHANGABLE CATIONS

EXCHANGEABLE CALCIUM AND MAGNESIUM : EDTA METHOD

Calcium and magnesium can be determined by complexometric titration with EDTA using Reader & Pattons reagent and Eriochrome Black-T as indicators at pH 12 and 10 respectively.

Reagents

1. **Hydrochloric acid (conc.)**
2. **Nitric acid (conc.)**
3. **EDTA Solution : 0.01 M :** Dissolve 3.722 gm EDTA in distilled water and dilute to 1000 ml with distilled water.
4. **Standard zinc acetate solution (0.01 M) :** Dissolve 0.2195 gm zinc acetate (AR) in water and dilute to 100 ml with distilled water.
5. **Buffer Solution (pH = 10)** : Dissolve 67.5 gm NH_4Cl in 510 ml ammonia solution and dilute to 1000 ml with distilled water.
6. **Buffer Solution (pH = 12) :** Dissolve 200 gm KOH in water and dilute to 1000 ml with distilled water.
7. **Buffer Solution (pH = 5.5) :** Dissolve 200 gms ammonium acetate in 30 ml acetic acid and dilute to 1000 ml with distilled water.
8. **Patton & Reader's Reagent :** Dissolve 0.1 gm in 100 ml methanol or water**.**
9. **Eriochrome Black-T :** Dissolve 0.1 gm in 100 ml methanol or water**.**
10. **Xylenol orange solution :** Dissolve 0.1 gm xylenol orange in 100 ml methanol/distilled water.
11. **Hydroxylamine hydrochloride solution :** 5% in distilled water**.**
12. **Triethanolamine solution :** 5% in distilled water.

Procedure

A.

- Take suitable aliquot from Ammonium acetate extract from Cation Exchange Capacity solution in 250 ml beaker.
- Evaporate to dryness on hot plate.
- Add 5 ml conc. HCl and dilute to 20 ml with distilled water.
- Add 1 ml conc. HNO_3.
- Allow to complete the reaction.
- Evaporate to dryness on hot plate.
- Extract with 1 ml conc. HCl, wash with distilled water, warm to dissolve any matter.
- Filter through Whatman No.40 filter paper if residue is present.
- Make up the volume of filtrate to 100 ml in volumetric flask.

(Note : Add 2 ml, 5% hydroxylamine hydrochloride and triethenolamine solutions to mask some interfering cations like Fe, Mn, Al, etc. before starting EDTA titration).

B. DETERMINATION OF CALCIUM AND MAGNESIUM

a. DETERMINATION OF CALCIUM + MAGNESIUM

- Take suitable aliquot of above solution in 250 ml beaker.
- Dilute to about 100 ml with distilled water.
- Add 20-25 ml buffer solution (pH = 10).
- Add 2-5 drops of Erio-chrome Black-T indicator.
- Titrate again 0.01 M EDTA solution.
- Peacock blue colour shows the end point of the reaction.
- Run blank in a same manner and deduct from sample titration.

b. DETERMINATION OF CALCIUM ONLY

- Take equal aliquot from the above solution in 250 ml beaker.
- Dilute to about 100 ml with distilled water.
- Add 20-25 ml buffer solution (pH=12).
- Add 2-5 drops of Patton & Reader's reagent indicator solution.
- Titrate against 0.01 M EDTA solution.
- Peacock blue colour shows the end point of reaction.
- Carry out blank in a similar manner and deduct from sample titration.

c. STANDARDIZATION OF EDTA AGAINST ZINC ACETATE SOLUTION

- Take suitable aliquot of standard zinc acetate solution (0.01 M) in 250 ml beaker.
- Dilute to 100 ml with distilled water.

- Add 20-25 ml buffer solution (pH=5.5).
- Add 2-5 drops of xylenol orange indication solution.
- Titrate against 0.01 M EDTA solution.
- Golden yellow colour shows the end point of the reaction.

Calculations

Calculate molarity of EDTA from standard formula of $N_1V_1 = N_2V_2$

$$\text{Exchangeable calcium : (meg/100 gm soil)} = \frac{\text{ml EDTA x MEDTA x ml aliquot x 100}}{\text{ml(original aliq.) x Wt. of sample}}$$

$$\text{OR} \quad \text{Ca,(meg/100 gm) soil} = \frac{\text{ml EDTA x MEDTA x ml aliquot x 100}}{\text{ml(original aliq.) x Wt. of sample x 20.04}}$$

(1 ml 1 MEDTA = 40.8 mg Ca = 24.3 mg Mg.)

Exchangeable magnesium

ml EDTA for Ca+Mg – ml EDTA for Ca = ml EDTA for Mg

$$\text{Exchangeable +Mg (meg/100 gm soil)} = \frac{\text{ml EDTA for Mg x MEDTA x ml aliquot x 100}}{\text{ml aliq. taken (original) x wt. x 12.15}}$$

DETERMINATION EXCHANGEABLE SODIUM & POTASSIUM

Reagents

Ammonium acetate (1N) pH = 7 : Dissolve 68 ml ammonium hydroxide solution in 58 ml acetic acid and dilute to 1000 ml with distilled water. Adjust pH to 7.

Procedure

- Take 5 gm soil sample in 100 ml conical flask.
- Add 25 ml 1N ammonium acetate buffer solution.
- Shake for about 5 minutes.
- Filter through Whatman No.41 filter paper.
- Use this filtrate for the determination of sodium and potassium.
- Feed above extract (filtrate) in Flame Photometer as per the instructions of instrument manufacturer and calculate comparing with standards.

Calculations

$$\text{Exchangeable sodium (meg/100 gm soil)} = \frac{\text{conc. from meter x aliquot x 100}}{\text{Wt. of sample x 23}}$$

{Note: (1 meg/L of Na = 0.023 gms of Na)
(1 meg/L of K = 0.019 gms of K)

DETERMINATION OF CALCIUM CARBONATE : ($CaCO_3$) (ACID NEUTRALIZATION METHOD) AND CALCIUM-BICARBONATES METHOD ($CaHCO_3$)

This is a rapid method for the determination of calcium carbonate in soil samples.

Reagents

1. **Sulphuric acid solution (0.4 N) :** Dilute about 11.12 ml of concentrated sulphuric acid (AR) and make up to 1000 ml with distilled water.
2. **Sodium hydroxide solution (0.4 N) :** Dissolve 16 gms of sodium hydroxide (AR) in water and dilute to 1000 ml with distilled water (Solution is to be standardized against standard acid solution).
3. **Phenolphthalein indicator :** Dissolve 0.1 gm in 100 ml distilled water.
4. **Methyl orange :** 0.1% solution in water.

STANDARDIZATION OF SULPHURIC ACID SOLUTION

- Take 0.1-0.2 gm sodium carbonate (AR) in 250 ml beaker.
- Add about 100 ml distilled water to dissolve it.
- Add 2-3 drops of methyl orange.
- Titrate against sulphuric acid solution.
- Purple colour shows the end point of the reaction.

$$N_{H2SO4} = \frac{\text{Wt. of } Na_2CO_3 \times 1000}{\text{Equi. Wt. of } Na_2CO_3 \times \text{ml, } H_2SO_4}$$

$$= \frac{\text{Wt. of } Na_2CO_3 \times 1000}{53 \times \text{ml, } H_2SO_4}$$

Procedure

- Take about 1-2 gm soil sample in 250 ml flask.
- Add 25 ml 0.4 N H_2SO_4 solution.
- Dilute to about 100 ml with distilled water.
- Boil for 5-10 minutes.
- Cool and titrate against standard NaOH solution using phenolphthalein as an indicator.
- Carry out blank in a similar manner.

Calculations

$$\% \, CaCO_3 = \frac{\{(\text{ml (Blank)} - \text{ml (exp)}\} \times N_{NaOH} \times 0.05 \times 100}{\text{Wt. of soil}}$$

Where : ml NaOH for blank sample
ml NaOH for experimental sample
(1 ml 1 N H_2SO_4 =0.05 gm of $CaCO_3$ = 1 ml 1 H NaOH)

DETERMINATION OF CALCIUM BICARBONATES (Ca HCO_3)

Procedure

- Take same solution from which calcium carbonate has been titrated.
- Add 2-4 drops of methyl orange indicator.
- Titrate further against same sulphuric acid solution till solution becomes red.
- Carry out blank in a similar manner and deduct from volume required for determination of $CaHCO_3$

Calculations

(1 ml 1 N H_2SO_4 = 0.101 gm of $CaCO_3$)

$$CaHCO_3(\text{meg/100 gm soil}) = \frac{\text{ml}_{CaHCO3} - \text{ml}_{CaCO3} \times N_1 \times 0.101 \times 100}{\text{Wt. of soil}}$$

DETERMINATION OF TOTAL NITROGEN IN SOIL SAMPLES

Total nitrogen can be determine in soil samples using salicylic acid method for the reduction of nitrogenous substances such as nitrite and nitrates into ammonium sulphate, which further converts into ammonia can be distilled off into boric acid solution and determined by titrimetric method.

Reagents

1. **Sulphuric acid :** conc. H_2SO_4
2. **Salicylic acid (AR/GR).**
3. **Sodium thiosulphate : (AR/GR).**
4. **Potasium sulphate : (AR/GR).**
5. **Copper sulphate : (AR/GR).**
6. **Sodium hydroxide :** 40% solution
7. **Methyl red indicator :** 0.05% in methanol/water
8. **Oxalic acid solution (0.1 N) :** Dissolve 0.63 gm oxalic acid (AR/GR) in water and dilute to 100 ml with distilled water.
9. **Sodium hydroxide solution (0.1 N) :** Dissolve 4 gm NaOH in water and dilute 1000 ml with distilled water.
10. **Sulphuric acid solution (0.1 N) :** Dilute 3.6 ml conc. H_2SO_4 in water and make up to 1000 ml with distilled water.

Procedure

- Take 4-5 gm finely powdered soil sample in Kjeldahl flask.
- Add 30 ml conc. H_2SO_4 containing 1 gm salicylic acid, mix thoroughly for 2-3 minutes and allow to stand for about half an hour to complete the reaction where formation of nitro salicylic acid is takes place.

- Add 5 gms sodium thiosulphate in above flask to reduce nitro-salicylic acid into amino-salicylic acid which further produces into ammonia. This ammonia is then absorbed by sulphuric acid producing ammonium sulphate.
- Add 5 gms potassium sulphate and 0.5 gm copper sulphate into the flask after 5-6 minutes.
- Digest the content of flask slowly on a heating divice until all the carbon gets oxidized.
- After completion of digestion, cool the mixture and dilute to 100-150 ml with water.
- Transfer the mixture into 500 ml round bottom flask.
- Pour 40 ml of 40% sodium hydroxide solution into above mixture and close it immediately.
- Distilled the content upto about its (1/3) one third of original volume.
- Collect distillate (ammonia) evolved during distillation in a measured quantity of standard sulphuric acid/boric acid solution.
- Titrate excess sulphuric acid/boric acid solution against standard sodium hydroxide solution using methyl red indicator.
- Carry out blank for the same volume.

Calculations

$$\text{Total Nitrogen \% in soil} = \frac{\text{ml NaOH consumed} \times N_{NaOH} \times 0.014 \times 100}{\text{Wt. of soil}}$$

(ml NaOH consumed = ml NaOH for blank – ml NaOH for soil samples)
(ml 1 N NaOH = 0.014 gms of Nitrogen)

DETERMINATION OF AMMONIUM NITROGEN IN SOIL SAMPLES

Ammonium nitrogen in soil sample can be determined by converting it into ammonia by the action of alkali solution and thus evolved ammonia is absorbed in dilute sulphuric acid solution taken in excess. The excess sulphuric acid can be titrated against standard sodium hydroxide solution from which a consumed volume of acid is calculated and ammonium nitrogen can be determined.

Reagents

1. **Magnesium oxide** : MgO (AR/GR)
2. **Potassium chloride :** Cl (AR/GR)
3. **Sulphuric acid (2%) :** 2 ml in 98 ml water.
4. **Standard sulphuric acid solution (0.1 N) :** 3.6 ml sulphuric acid is diluted to 1000 ml. (can be standardized against standard sodium hydroxide solution using phenolphthalein indicator).
5. **Oxalic acid solution (0.1 N) :** 0.63 gm oxalic acid in 100 ml distilled water**.**

6. **Methyl red indicator** : (0.05%) in methanol/water**.**
7. **Phenolphthalein indicator :** (1%) in water/methanol**.**

Procedure

- Take 10-20 gm finely powdered soil sample in 250 ml Erlenmeyer flask.
- Add 5 gms magnesium oxide, mix.
- Add 0.5 gm potassium chloride, mix again.
- Add about 100 ml distilled water into the flask.
- Fix immediately to the Kjeldahl distillation unit to prevent ammonia to escape.
- Shake the flask carefully and distilled ammonia using heating device.
- Collect distillate (ammonia) in 50 ml 2% sulphuric acid solution.
- Titrate collected ammonia in excess of sulphuric acid solution against standard sodium hydroxide solution using methyl red indicator.
- Carry out blank of same volume of sulphuric acid against same standard sodium hydroxide solution.
- Sodium hydroxide can be standardized by titrating against standard oxalic acid solution using phenolphthalein as an indicator**.**

Calculations

$$\text{Amm.Nitrogen \% in soil} = \frac{\text{ml NaOH(Blank)} - \text{ml NaOH (sample)} \times N_{NaOH} \times 0.014 \times 100}{\text{Wt. of soil sample}}$$

(ml NaOH consumed = ml NaOH (Blank) – Ml NaOH (Sample)

(1 ml 1 N NaOH = 0.014 gms of Nitrogen & N x 1.2143 = NH_3)

DETERMINATION OF NITRATE NITROGEN IN SOIL SAMPLE

In this method nitrate has been converted to ammonia, which is absorbed in excess dil. Sulphuric acid and remaining excess acid can be determined by titrating against standard alkali solution (i.e. sodium hydroxide solution).

Reagents

1. **Sodium hydroxide : (**1%) Dissolve 1 gm in 100 ml distilled water**.**
2. **Standard sodium hydroxide solution (0.1 N) :** Dissolve 4 gm NaOH in water and dilute to 1000 ml with distilled water. Standardized with standard oxalic acid (0.1 N) using phenolphthalein as an indicator.
3. **Sulphuric acid solution (2%) :** Add 2 ml sulphuric acid in distilled water and dilute to 100 ml.
4. **Standard sulphuric solution (0.1 N) :** 3.6 ml conc. sulphuric acid is diluted to 1000 ml and standardized against standard alkali solution.
5. **Oxalic acid solution (0.1 N) :** Dissolve 0.63 gm oxalic acid in water and dilute to 100 ml distilled water.
6. **Devardas Alloy (Cu:50%, Al:45% and Zn:5%)**

7. **Phenolphthalein indicator :** 1% in water/methanol
8. **Methyl red indicator** : 0.1% in water/methanol**.**

STANDARDIZATION OF SODIUM HYDROXIDE SOLUTION AGAINST STANDARD OXALIC ACID SOLUTION

- Take aliquot of 0.1 N NaOH solution in 250 ml beaker.
- Dilute to about 100 ml with distilled water.
- Add 2-3 drops of phenolphthalein indicator.
- Titrate against 0.1 N oxalic acid solution.
- Disappearance of red colour shows the end point.

Calculations

$$N_{NaOH} = \frac{\text{N oxalic acid x ml oxalic acid required}}{\text{ml NaOH taken (aliquot)}}$$

STANDARDIZATION OF SULPHURIC ACID AGAINST STANDARD SODIUM HYDROXIDE ACID SOLUTION

- Take suitable aliquot of sodium hydroxide solution in 250 ml beaker.
- Add distilled water to dilute to about 100 ml.
- Add 2-3 drops of phenolphthalein indicator.
- Titrate against sulphuric acid solution.
- Disappearance of red colour shows the end point.

Calculations

$$N_{H2SO4} = \frac{N_{NaOH} \text{ x ml (NaOH aliquot)}}{\text{ml } H_2SO_4 \text{ required}}$$

Procedure

- Take residue remained after the determination of ammonium nitrogen in the same flask.
- Add 1 gm Devardas alloy.
- Add 25 ml 1% NaOH in to the flask.
- Keep this mixture on a distillation unit and allow to stand for over night.
- Evolved ammonia is absorbed in 50 ml of 2% H_2SO_4 through condenser of kjeldahl distillation unit.
- Next day, distill the mixture. Allow ammonia evolved to absorb in sulphuric acid as mentioned above.
- Take sulphuric acid (ammonia absorbed) or make up the volume as you feel suitable.
- Add 2-3 drops of phenolphthalein indicator.

- Titrate against standard sodium hydroxide solution.
- Disappearance of red colour shows the end point.
- Carry out blank titration of the same volume of sulphuric acid taken for sample.

Calculations

$$NO_3\text{-N}\ \% = \frac{\text{ml NaOH (Blank)-ml NaOH (sample) x N x 100 x 0.014 x 100}}{\text{Wt. of sample (gms)}}$$

Where N = Normality of NaOH

OR If aliquot is taken then

$$NO_3\text{-N}\ \% = \frac{\text{ml NaOH (A) - ml NaOH(B) x gms } NO_3\text{-N aliquot x N x 100 x 0.014}}{\text{Wt. of sample in aliquot(gms)}}$$

A=ml NaOH in blank
B=ml NaOH in sample
OR

$$NO_3\text{-N}\% = \frac{\text{ml } H_2SO_4 \text{ (for Sample)-ml } H_2SO_4 \text{ (for Blank) x N x 0.014 x 100}}{\text{Wt. of sample (gms)}}$$

DETERMINATION OF AVAILABLE PHOSPHOROUS IN SOIL SAMPLES

A portion of phosphorous, which is utilized by the plant directly, is known as available phosphorous. This can be determined by two methods i.e. phosphorous soluble in sodium bicarbonate and phosphorous soluble in dilute acid-fluoride.

DETERMINATION OF PHOSPHOROUS SOLUBLE IN SODIUM BICARBONATE (OLSEN-BICARBONATE METHOD)

Here phosphorous can be extracted from soil with sodium bicarbonate solution at pH = 8.5.

Reagents

1. **Extracting solution (sodium bicarbonate solution) (0.5 M) :** Dissolve 42 gms $NaHCO_3$ (sodium bicarbonate) in water and dilute to 1000 ml with distilled water, adjust pH = 8.5.
2. **Sulphuric acid (5N) :** Add 141 ml conc. H_2SO_4 in 500 ml water and dilute to 1000 ml after cooling.
3. **Stannous chloride solution (0.1%)** : Dissolve 0.1 gm stannous chloride in 5 ml conc. HCl and dilute to 100 ml with distilled water.

4. **Ammonium Molybdate solution (1% in 4 N H_2SO_4) :** Dissolve 10 gm ammonium molybdate (AR) in 25 ml distilled water with warming. Cool and add about 110 ml conc. H_2SO_4. Dilute to 1000 ml.
5. **P-nitrophenol solution (0.25%) :** Dissolve 0.25 gm P-nitrophenol in water and dilute to 100 ml with distilled water.
6. **Standard stock phosphate solution :** Dissolve 0.4393 gm pot. dihydrogen phosphate KH_2PO_4 (AR) in water and dilute to 1000 ml with distilled water. (1 ml = 0.1 mg P).
7. **Standard phosphate solution :** Dilute 10 ml of stock phosphate solution of 1000 ml with distilled water. (1 ml = 1 ug P).

PREPARATION OF STANDARD GRAPH

- Take suitable aliquots from standard phosphate solution ranging from 0-10 ug P in 100 ml volumetric flask.
- Adjust pH = 5 (can be checked using universal pH indicator paper).
- Add 5 ml ammonium molybdate solution in each flasks mix.
- Add 0.25 ml stannous chloride solution, mix again.
- Make the volume to 100 ml with distilled water and shake thoroughly.
- Measure absorbances/transmittances at 660 nm and blank solution.
- Plot graph between absorbances/transmittances against concentrations of phosphorous.

Procedure

- Take 2-5 gms of soil sample in 250 ml conical flask.
- Add 100 ml sodium bicarbonate solution into the conical flask.
- Shake a flask for about 30 minutes.
- Filter after 30 minutes through Whatman No.40 filter paper.
- If filtrate has colour, add a pinch of carbon black. Shake for some time to remove colour and filter again through Whatman No.40 filter paper.
- Make up the volume of filtrate in 100 ml volumetric flask.
- Take suitable aliquot from the above prepared solution in 100 ml volumetric flask.
- Adjust pH = 5 by adding acid/alkali solutions.
- Add 5 ml ammonium molybdate solution, mix.
- Add 0.25 ml stannous chloride solution, mix again.
- Make the volume to 100 ml with distilled water and mix thoroughly.
- Allow to stand for 10 minutes.
- Measure the absorbance/transmittance at 660 nm.
- Carry out blank in a similar manner.
- Find the concentration of phosphorous from the standard graph.

Calculations

$$P\ \% = \frac{\text{mg. P (from graph) in aliquot x 100}}{\text{Wt. of sample (gm) x 1000 (in aliquot)}}$$

$$= \frac{\mu\text{g.P (in aliquot) x 100}}{\text{Wt. of sample in aliquot (gms) x 1000 x 1000}}$$

DETERMINATION OF PHOSPHOROUS SOLUBLE IN DILUTE ACID FLUORIDE (BRAY'S METHOD)

The method is suitable for the determination of phosphorous in acidic soil samples.

Reagents

1. **Ammonium Fluoride Solution (1 N NH_4F) :** Dissolve 37 gms of NH_4F in distilled water and dilute to 1000 ml with distilled water**.**
2. **Hydrochloric acid (0.5M):** Dilute 40.4 ml conc. hydrochloric acid to 1000 ml with distilled water.
3. **Extracting solution :** Mix 32.60 ml of 1N NH_4F solution and 54.4 ml of 0.5 HCl solution and dilute to 1000 ml with distilled water.
4. **Stannous chloride solution :** Dissolve 0.12 gm stannous chloride in 2.5 ml conc. hydrochloric acid by warming and dilute to 100 ml with distilled water.
5. **Standard phosphorous solution :** Dissolve 0.4393 gm KH_2PO_4 in distilled water and dilute to 1000 ml with distilled water (1 ml = 0.1 mg P = 100 ug P).
6. Dilute 10 ml. 100 ug P to 100 ml with distilled water.(1 ml = 0.01 mg P = 10 ug P).
7. **Ammonium Molybdate Solution :** (1.5% in 35% HCl) : Dissolve 15 gm ammonium mylybdate in 350 ml conc. HCl and dilute to 1000 ml with water.

PREPARATION OF STANDARD GRAPH

- Take suitable aliquots from the standard phosphorous solution ranging from 0-10 ug P in 100 ml volumetric flask.
- Add 2 ml ammonium molybdate solution in each flask, mix.
- Add 1 ml of stannous chloride solution, mix again.
- Make up the volume to 100 ml with distilled water, mix thoroughly.
- Measure absorbances/transmittances at 660 nm. after 10 minutes
- Carry out bank in a similar manner.
- Plot standard graph between absorbances/transmittances and the concentrations of phosphorous.

Procedure

- Take 1-2 gm soil sample into a 100 ml beaker.
- Add 7-14 ml extracting solution into beaker.

- Shake for 1-2 minutes.
- Filter through Whatman No.40 filter paper.
- Take filtrate for determination of phosphorous. (Make up the volume if phosphorous content is more and take aliquot from this solution).
- Take suitable aliquot from extracted solution in l00 ml volumetric flask.
- Add 2 ml ammonium molybdate solution, mix.
- Add 1 ml stannous chloride solution, mix again.
- Make up the volume to 100 ml with distilled water, mix thoroughly.
- Measure absorbance at 660 nm after 10 minutes.
- Carry out blank in a similar manner**.**

Calculations

$$\% P = \frac{\text{mg. P (from graph) in aliquot x 100}}{\text{Wt. of sample in aliquot (gm) x 1000}}$$

$$= \frac{\mu\text{g.P (in aliquot) x 100}}{\text{Wt. of sample in aliquot (gms) x 1000 x 1000}}$$

DETERMINATION OF TOTAL SULPHUR IN SOIL SAMPLES

Total sulphur can be determined by converting sulphur into sulphate by using oxidizing agent and analysed by colorimeteric method.

Reagents

1. **Digesting Solution :** Dissolve 100 gms pot. Nitrate (KNO_3) in water and add 350 ml conc. nitric acid and dilute to 1000 ml with distilled water**.**
2. **Nitric Acid Solution : (25%) :** 250 ml conc. nitric acid is diluted to 1000 ml with distilled water.
3. **(a) Hydrochloric acid (6N):** Dilute 484 ml conc. hydrochloric acid to 1000 ml with distilled water.
   (b) Sulphate Sulphur (SO_4-S) Solution : (10 PPM) : Dissolve 0.0544 gms pottasium sulphate (K_2SO_4) in 1000 ml 6 N HCl.
4. **Barium Chloride $BaCl_2$ (AR/GR) :** Crystals.
5. **Standard Stock Solution :** Dissolve 0.4218 gm K_2SO_4 in water and dilute to 1000 ml with distilled water (1 ml = 0.10 mg SO_4-S = 100 μg SO_4-S).
6. **Standard SO_4-S Solution :** Dilute 10 ml 100 ug SO_4-S solution to 100 ml with distilled water (1 ml = 10 μg SO_4-S).

PREPARATION OF STANDARD GRAPH

- Take suitable aliquot of above standard SO_4-S solution in the range of 0 to 100 μg SO_4-S in 100 ml volumetric flask.
- Add 0.25 gm barium chloride (AR), in each volumetric flask, swirl to dissolve.

- Add 1 ml (6N HCL + 10 ppm SO_4-S) (seed) solution and allow to stand for 1 minute.
- Again swirl the content in the flask.
- Make up the volume to 100 ml with distilled water.
- Take absorbances/transmittances at 420 nm after 3 minutes.
- Plot a graph between absorbances and SO_4-S concentrations.

Procedure

- Take 1-2 gm dried fine soil sample in 250 ml beaker.
- Add 10 ml digesting solution.
- Keep on water bath and allow to evaporate upto dryness.
- Replace beaker and allow to cool.
- Add 5 ml of 25% Nitric acid solution.
- Digest the content for one hour on steam bath.
- Dilute to about 50 ml with distilled water.
- Filter through Whatman No.40 filter paper.
- Transfer the filtrate into 100 ml volumetric flask and make up with distilled water.
- Take suitable aliquot of above filtrate or whole solution for determination of SO_4-S as you feel convenient.
- Add 0.25 gm barium chloride (AR) crystals, swirl to dissolve.
- Add 1 ml of (6 N HCl + 10 ppm SO_4-S solution (seed).
- Swirl contents for about 1 minute.
- Make up the volume to 100 ml, mix well.
- Take absorbance at 420 nm after 3 minutes.
- Carry out blank in a similar manner.

Calculations

$$\% \, SO_4\text{-S} = \frac{\mu g, \, SO_4\text{-S in aliquot}}{\text{wt. of sample in aliquot (gms) x}10^9}$$

OR

$$\% \, SO_4\text{-S} = \frac{.\ \mu g, \, SO_4\text{-S in aliquot}}{\text{wt. of sample in aliquot (gms) }10^7}$$

DETERMINATION OF AVAILABLE SULPHUR IN SOIL SAMPLE

Sulphur can be determined using turbidimetric/colorimetric methods by formation of suspension with barium chloride to form barium sulphate.

Reagents

1. **Phosphorous Extraction Solution (500 ppm) :** Dissolve 2.195 gms potassium dihydrogen orthophosphate (KH_2PO_4) in water and dilute to 1000 ml with distilled water.

2. **Nitric acid (25%) :** 25 ml conc. HNO_3 is diluted to 100 ml water**.**
3. **Acetic acid phosphoric acid mixture :** 300 mlAcetic acid and 100 ml phosphoric acid is mixed together.
4. **Gum-Acacia-Acetic Acid Solution :** Dissolve 5 gms. Gum-acacia in hot water. Cool filter through Whatman No.42 filter paper if precipitate appears. Dilute filtrate to 1000 ml with distilled water**.**
5. **Standard stock sulphate solution :** Dissolve 0.545 gms potassium sulphate (AR/GR) in water and dilute to 1000 ml with distilled water. (1 ml = 0.10 mgS = 100 μgS).
6. **Standard working solution :** Dilute 10 ml 1000 ugs solution to 1000 ml with distilled water. (1 ml = 10 μgS).
7. **Barium chloride :** $BaCl_2$ (AR/GR) Crystals**.**
8. **Barium sulphate seed suspension :** Dissolve 20.45 gm of Barium Chloride in 50 ml hot distilled water. Add 0.5 ml stock sulphate solution, mix. Heat to boiling, cool. Add 5 ml of Gum acacia-acetic acid solution, mix again.

(Note this suspension) is not stable hence it should be prepared freshly).

PREPARATION OF STANDARD GRAPH

- Take suitable aliquots of standard sulphur solution ranging from 0-20 μgS in 25 ml volumetric flask.
- Add 2.5 ml of 25% nitric acid in each flask, mix.
- Add 2 ml acetic acid-phosphoric acid solution, mix well.
- Add 0.5 ml barium sulphate seed suspension, mix well.
- Add 0.2 gm (or pinch) barium chloride crystals in mixture and shake for about 5 minutes.
- Add 1 ml gum-acacia solution after 5 minutes and make up the volume to 25 ml with distilled water, mix well again. Allow to stand for about ½ hour.
- Measure the absorbances/transmittances at 440 nm.
- Plot a graph between absorbances/transmittances and concentrations of sulphur.

Procedure

- Take about 20 gm dried fine soil sample in 250 ml conical flask.
- Add 100 ml of 500 ppm phosphate extraction solution, shake for about ½ an hour.
- Filter through Whatman No.42 filter paper.
- Take above filtrate for determination of sulphur content in soil using complete filtrate or making up volume of it.
- Take suitable aliquot (if volume is make up) in 25 ml volumetric flask.
- Add 2.5 ml of 25% nitric acid solution, mix.
- Add 2 ml acetic acid-phosphoric acid solution, mix again.
- Add 0.5 ml barium sulphate acid suspension, mix well.
- Add 0.2 gm (pinch) barium chloride (AR). Shake the contents for 5 minutes.

- Add 1 ml gum-acacia solution after 5 minutes.
- Make up the volume with water and mix well again.
- Allow to stand for ½ an hour.
- Take absorbance/transmittance at 440 nm.
- Carry out blank in a similar manner and deduct from sample reading.

Calculations

$$\%S = \frac{\mu g\ S\ (\text{from graph in aliquot}) \times 100}{\text{Wt. of sample in aliquot (gm)} \times 10^9}$$

$$= \frac{\mu g\ S\ (\text{in aliquot from graph})}{\text{Wt. of sample in aliquot (in gm)} \times 10^7}$$

DETERMINATION OF MERCURY IN SOIL SAMPLES

Mercury can be determined by using Mercury Analyser at the trace level in soil samples.

Reagents

1. **Aqua-Regia** : Mix 1 part of Nitric acid and 3 parts of Hydrochloric acid (conc. HNO_3 + : Conc. 3HCl).
2. **Potassium Permanganate Solution (5%) :** Dissolve 5 gms $KMnO_4$ (Pot. permanganate) in 100 ml distilled water.
3. **Potassium Persulphate Solution (5%) :** Dissolve 5 gm pottasium persulphate ($K_2S_2O_8$) in 100 ml distilled water.
4. **Hydroxylamine hydrochloride solution (20%) :** Dissolve 20 gm hydroxylamine hydrochloride (NH_2OH – HCl) in 100 ml conc. hydrochloric acid.
5. **Stannous chloride solution (20% in 50% HCl) :** Dissolve 30 gms stannous chloride in 50 ml conc. hydrochloric acid and dilute to 100 ml with distilled water.
6. **Standard Stock Mercury Solution :** Dissolve 0.1354 gms mercuric chloride ($HgCl_2$) in 2% HNO_3 and dilute to 1000 ml, (1 ml = 100 ppm Hg.).
7. Dilute 10 ml 100 ppm stock mercury solution to 1000 ml add 2% HNO_3 solution. (1 ml = 1 ppm = 1000 μg Hg).
8. Dilute 10 ml 1000 μg Hg solution to 1000 ml adding 2% HNO_3 solution (1 ml = 10 μg Hg). OR Dilute 10 ml, 1000 μg Hg solution to 100 ml adding 2% HNO_3 solution (1 ml = 100 μg Hg)

This solution can be taken for standardization**.**

PREPARATION OF STANDARD GRAPH

- Take suitable aliquot of standard mercury solution ranging from 0-500 ug Hg in 300 ml B.O.D. bottle (Mercury generator bottle).
- Add distilled water so that the total volume of solution should be 100 ml (including all reagents).

- Add 5 ml stannous chloride, which includes in 100 ml total volume of BOD bottle.
- Place a magnetic bar inside the bottle.
- Keep the BOD bottle on magnetic stirrer and allow to stir for a fixed period (5 minutes).
- Before this check mercury analyzer as per the manufacturer’s instructions and keep ready for taking the readings.
- After fixed period, i.e. 5 minutes, start the pump and measure the absorbances of mercury shown on the meter.
- Feed blank and deduct from every reading.
- Plot a graph between absorbances and the concentrations of mercury in ug of Hg.

Procedure

- Take about 1-5 gm finely powder soil sample in 100 ml beaker.
- Add 25 ml aqua-regia in beaker.
- Keep for about ½ an hour by swirling occasionally.
- Heat on water bath for about 2 hours with swirling occasionally.
- Cool at room temperature.
- Add 25 ml, 5% $KMnO_4$ solution, mix.
- Add 2 ml, 5% $K_2S_2O_8$ solution, mix again.
- Allow to stand for overnight for reaction.
- Next day add 20% hydroxylamine hydrochloride solution drop wise to oxidize $KMnO_4$ solution completely.
- Filter through Whatman filter paper No.40.
- Wash with distilled water.
- Make up the volume to 100 ml or take complete solution for the determination of mercury depending upon the quantity of mercury present in soil sample.
- Take aliquot or complete solution as prepared above in 300 ml BOD bottle.
- Add distilled water to make fixed volume as done in standard graph.
- Add 5 ml stannous chloride solution which includes in fixed volume (total volume = 100 ml.).
- Place one stirring bar inside the BOD bottle.
- Keep on magnetic stirrer and allow to continue for fixed time (5 minutes).
- After five minutes take absorbance on meter.
- Find out the concentration of mercury from the standard graph.
- Carry out blank and deduct from reading.

Calculations

$$\% \text{ Hg in soil} = \frac{\text{conc. Hg } (\mu g) \text{ in aliquot x } 100}{\text{Wt. of soil in aliquot (gms) x } 10^9}$$

DETERMINATION OF TRACE/HEAVY ELEMENTS IN SOIL SAMPLES

Soil samples (fine powder –100 mesh) is used for the dissolution of trace/heavy elements in aqua-regia solution and can be analysed using appropriate instruments for analysis of them.

Reagents

1. **Hydrochloric acid :** Conc. Hydrochloria acid (AR) grade**.**
2. **Nitric acid : Conc.** Nitric acid. AR grade**.**
3. **Nitric acid 0.5 M :** Dilute 32 ml conc. HNO_3 to 1000 ml with distilled water.

Procedure

- Take about 5 gms of finely powder soil sample in 250 ml beaker.
- Add 21 ml conc. hydrochloric acid, swirl.
- Add 7 ml conc. nitric acid, swir well again.
- Digest the content on hot plate for about 1-2 hours with covering in fume cupboard.
- Cool and filter through Whatman No.40 filter paper.
- Wash with hot distilled water.
- Collect the filtrate and make up the volume in 100 ml volumetric flask with distilled water.
- Use above volume for determination of trace/heavy elements using appropriate instrument such as Atomic Absorption Spectrophotometer, Inductively coupled plasma Analyser, etc.

Calculations

Calculate the concentrations of each trace heavy elements and express either in ppm or percentage as applicable.

6.28 AMBIENT AIR QUALITY MONITORING

In a system of Ambient Air Quality monitoring commonly “High volume Sampler” (HVS) is used. Using this instrument (HVS) Suspended Particulate Matter (SPM), i.e. Respirable SO_2 and NO_x can be determined in a single instrument.

For the sampling purpose HVS are installed around dust producing sources/points and measurements are carried out for a fixed period depending upon the concentration of dust so that the sufficient amount of dust is collected on initially weighed filter paper (Whatman Glass Micro Fibre Filter Paper) GF/A of size 203 x 284 mm. The time period can be varied if the concentration of dust is very less, then 16 or 24 hours can sampled and if the concentration of dust is much more 4-6 hours but commonly 8 hours has been considered as a standard for the collection of Suspended Particulate Matter (SPM).

After collection of a sufficient dust for the specific period, the filter paper is re-weighed and the difference in both weights are calculated. At the same time we have to note the initial, final volume of air passed through the instrument to calculate the concentration of SPM per cubic meters of air passed during the sampling.

After removal of dust (SPM) in a same instrument clean air is passed through the impingers containing NaOH solution and sod.tetra-chloromercurate solution in series so that NO_x and SO_2 gases can be absorbed respectively. After absorption of NO_x and SO_2 gases in the solutions these can be analysed using appropriate methods of analysis. Generally, spectrophotometric methods for analysis are most suitable.

Calculations : Suspended Particulate Matter (SPM)

The volume of air sampled can be calculated using a formula :

$$V = \frac{(Q_i + Q_f)}{2} \times T$$

Where V = Volume of air sampled, m^3/min
Q_i = initial flow rate of air m^3/min
Q_f = final flow rate of air m^3/min
T = Total time of sampling in minutes

and the mass concentration of SPM can be calculated as :

$$SPM \ ug/m^3 = \frac{(W_f - W_i)}{V} \times 10^{-6}, \mu g/m^3$$

Where, W_f = final weight of paper + sample
W_i = initial weight of paper
V = total volume of air sampled, m^3

GASEOUS POLLUTANTS ANALYSIS

Gaseous pollutants (NO_x & SO_2) are absorbed in specific absorbing reagents at an average flow rate of 0.6 to 1.l/min. NO_x is absorbed in 0.10 M NaOH solution while SO_2 is absorbed in 0.10 M sod.tetra-chloromurcurate solution. 30 ml of respective absorbing solutions are taken in each impingers.

ANALYSIS OF NITROUS OXIDES (NO_X) :

A sample is collected by bubbling air from HVS through 30 ml of 0.10 M sod.hydroxide solution. Loss in volume due to evaporation is make up to 30 ml and an aliquot is taken for analysis.

Principle

Oxides of Nitrogen as NO_2 (Nitrogen dioxide) is absorbed quantitatively by bubbling air through a NaOH solution (Sod.Hydroxide) which form a stable sodium Nitrite NO_2 + NaOH ---- $NaNO_2$ (stable sod.nitrite solution).

Thus $NaNO_2$ (sod.nitrite) produced as above can be determined spectrophotometric method by developing coloured complex by adding appropriate reagents and measurement taken is at 540 nm and compared with standards from which a concentration of NO_x present in the sampled air is calculated.

Reagents

1. **Absorbing Reagent : (0.10 N NaOH) :** Dissolve 4.0 gms sod.hydroxide in distilled water and dilute to 1000 ml.
2. **Sulphanilamide solution :** 20 gm sulphanilamide is dissolved in 700 ml distilled water, add to this 50 ml of H_3PO_4 (Phosphoric acid 85%) slowly while stirring and dilute to 1000 ml with distilled water. Keep in refrigerator. This can be used up to one month.
3. **NEDA solution :** Dissolve 1.0 gm N (1-naphthyl) ethylene diamine dihydrochloride (NEDA) in 1000 ml distilled water. Keep in refrigerator to protect from sunlight. This solution can be used up to one month.
4. **Hydrogen Peroxide :** 1 ml of 30% hydrogen peroxide is diluted to 1000 ml. Keep in refrigerator to protect from light.
5. **Standard Sodium Nitrite Solution** : Dissolved 0.135 gm sodium Nitrite (AR/GR) in water and dilute to 1000 ml with distilled water.

   1 ml of above solution = 90 μg NO_2 = 100 μg NO_2 gas

PROCEDURE FOR COLOUR DEVELOPMENT

10 ml aliquot from the original solution is taken in 30 ml graduated cylinder.

- Add 1 ml H_2O_2 solution. Mix the content.
- Add 10 ml sulphanilamide solution – Mix again.
- Add 1 ml NEDA solution. Mix/shake the contents thoroughly, make up volume to 25 ml, and allow to develop a colour for about 10 minutes.

Take a blank in a same manner. Measure an absorbance after 10 minutes at 540 nm using spectrophotometer. Find out the concentration from the standard/calibration graph and calculate the concentration of NO_2/ml.

STANDARDIZATION AND CALIBRATION FOR NO_2 :

Take 1.0, 2.0, 3.0……10.0 ml standard solution of sod. Nitrite in 30 ml graduated cylinders.

- Add 1 ml H_2O_2 solution in each cylinder.
- Add 10 ml sulphanilamide solution.
- Add 1 ml NEDA solution. Mix thoroughly and make up the volume to 25 ml of each cylinder. Allow to develop a colour for 10 minutes and measure an absorbances at 540 nm using Spectrophotometer against reagent blank.

Plot a graph of concentrations (μg) against absorbance and find the concentration of the experimental solutions.

Calculations

$$NO_2\text{, ug/ml} = \frac{NO_2\text{, }\mu\text{g/ml}}{10\text{ ml (i.e. aliquot)}}$$

$$\text{and } NO2\text{, ug/m3} = \frac{NO_2\text{, }\mu\text{g/ml} \times 30 \text{ (i.e. Volume taken for absorbing reagent)}}{V \text{ (i.e. total volume of air)}}$$

$$V = \frac{(Q_i + Q_f)}{2} \times T$$

Where V = Volume of air sampled, m^3
Q_i = Initial flow rate of air, m^3/min
Q_f = Final flow rate of air, m^3/min.
T = Total time in minutes.

{Note :- If the weights are taken in grams, then

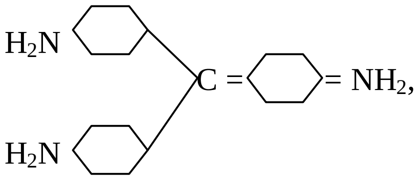
$$NO2\text{, ug/m3} = \frac{NO2\text{, }\mu\text{g/ml} \times 30 \quad \times \quad 10\text{-}6\}}{V}$$

ANALYSIS OF SULPHUR DIOXIDE

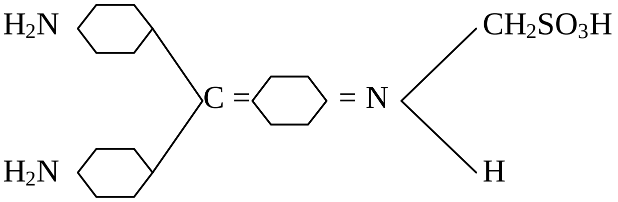
For the determination of SO_2 (sulphur dioxide) a sample is collected by bubbling through an aqueous solution of sodium tetra-chloro-mercurate, which can absorb SO_2 quantitatively.

Principle

Sodium tetra-chloromercurate (TCM) absorbs SO_2 quantitatively and formed a dichlorosulphito mercurate complex, after addition of formaldehyde and P-rosaniline at a controlled pH = 1, a coloured complex of P-rosaniline-methylsulphonic acid is formed which can be measured at 560 nm.

$HgCl_2SO_3^{-2} + H_2CO + 2H^+$ + 

which gives



$+ 2Cl^- + H_2) + Hg^{+2}$

Reagents

1. **Absorbing Reagent** : 0.10 M sodium tetra-chloromercurate (TCM). Dissolve 27.2 gms Mercuric chloride and 11.7 gms sodium chloride in water and dilute to 1000 ml with distilled water.
2. **Para-Rosaniline Hydrochloride :** Dissolved 0.2 gm of P-rosaniline hydrochloride in water and dilute to 100 ml with distilled water. Allow to stand for 48 hours. Filter if precipitate appears.
3. Take above 20 ml of P-rosaniline hydrochloride solution, add 6 ml conc. HCl, allow to stand for 5 min. and make up the volume to 100 ml.
4. **Formaldehyde solution : (0.2%) :** Dissolve 5 ml of 40% formaldehyde solution to 1000 ml with distilled water.
5. **Sulphamic Acid Solution** : Dissolve 0.6 gm sulphamic acid in 100 ml distilled water.

PROCEDURE FOR COLOUR DEVELOPMENT

A 10 ml aliquot is taken from the original solution in 30 ml graduated cylinder.

- Add 1 ml sulphamic acid solution (masking agent for NO_x).
- Add 1 ml p-rosaniline solution. Mix well.
- Add 1 ml formaldehyde solution. Mix thoroughly the contents and allow to stand for 10 minutes to stabilize the colour of the complex.

Measure the absorbance/concentration after 10 min. at 560 nm using spectrophotometer. Concentration of SO_2 can be calculated from the standard graph.

STANDARDISATION AND CALIBRATION

A. Preparation of standard sulphite solution

- Dissolve 0.4 gm Na_2SO_3 (Sod.Sulphite) in water and dilute to 500 ml.
- Take 25 ml aliquot from above solution in 250 ml conical flask. Dilute it to about 100 ml with distilled water.
- Add 50 ml of 0.01 N iodine solution and cover immediately and allow to stand for five minutes.
- Titrate the content with 0.01 N sod.thiosulphate solution using starch as an indicator. Change of blue colour to colourless shows the end point of the reaction.
- Carry out a bank in a same manner.

Calculate the concentration of SO_2 in ug/ml using a formula :

$$SO_2\text{, ug/ml} = \frac{\text{(A-B) ml x N x 32,000}}{\text{Aliquot of standard solution}}$$

Where : A = Volume in ml of thiosulphate for blank
B = Volume in ml of thiosulphate for sample
N = Normality of sod.thiosulphate
32,000 equivalent for SO_2

B. **Preparation of calibration graph :**

- Dilute 2 ml of above standard solution to 100 ml with TMC solution.
- Take aliquots of 1 ml, 2 ml, 3 ml, 4 ml & 5 ml from above solution in a graduated cylinder of 30 ml capacity.
- Add 1 ml of sulphamic acid solution to each cylinder.
- Add 1 ml P-rosaniline solution.
- Add 1 ml formaldehyde solution, mix the contents thoroughly and make up the volume to 20 ml with TMC (Tetra-chloromercurate) solution. Mix again and allow to stand for 10 minutes to develop and stabilize the colour.

Measure Absorbance/concentrations using a spectrophotometer at 560 nm against a blank prepared in a same manner.

Plot a standard graph between Absorbance and concentrations.

Calculations

$$SO_2\text{, }\mu\text{g/ml} = \frac{SO_2\text{, }\mu\text{g/ml}}{\text{10 ml (i.e. aliquot taken)}}$$

$$\text{and } SO_2\text{, }\mu\text{g/m}^3 = \frac{SO_2\text{, }\mu\text{g/ml x 30 (i.e. Total vol. Taken of Absorbing Reagent)}}{\text{V (Total Volume of air)}}$$

$$V = \frac{(Q_i + Q_f)}{2} \times T$$

Where V = Volume of air sampled, m^3
Q_i = Initial flow rate of air, m^3
Q_f = Final flow rate of air, m^3
T = Total time in minutes.

(Note : If weights are taken in grams, then

$$\mathrm{So_2}, \mu g/m^3 = \frac{\mathrm{SO_2}, \mu g/ml \text{ x } 30}{V} \text{ x } 10^{-6})$$

Addenda 1

BORON ORES

The chief minerals of Boron are Ascharite ($MgHBO_3$), Sassolite $B(OH)_3$, Ludwigite $(MgFe)_2Fe[BO_3]O_2$, Borax $Na_2B_4O_7.10H_2O$, Inderite $Mg_2B_6O_{11}.15H_2O$, Colemanite $CaB_6O_{11}.5H_2O$ and Calcioborite $Ca_5B_8O_{17}$, Boronatrocalcite $NaCaB_3O_9.8H_2O$.

Boron is generally analysed for B_2O_3, Fe_2O_3 ,Al_2O_3 ,CaO, MgO, Na_2O ,K_2O and LOI.

Determination of SiO_2 and preparation of Stock solution

Weigh 0.5 g of sample in a 200 ml silica dish. Add 10 ml of HCl and 2 ml HNO_3.Digest and evaporate over a moderately low flame. Expel all liquid from the dish. Remove the dish from the flame and cool it. Add 4-5 drops of dilute sulphuric acid. Add 10 ml methanol. Ignite the methanol with open flame. Stir the mass. Apple green flame will indicate the presence of borate in the mass. Cool the dish. Again repeat the process of removal of borate by additional quantity of sulphuric acid and methanol till all borate is removed.

Cool the mass; add 5 ml concentrated hydrochloric acid and 50 ml demineralised water. Boil the content on burner. Cool and filter through Whatman 40.Wash the residue 5-6 times with hot water. Preserve the filtrate for estimation of other radicals. Transfer the filter paper into a platinum crucible. Ignite this at $1000^{o}C$ in a muffle furnace. Cool the mass in a desiccator and weigh .Moisten the mass with little DM water. Add 2-3 drops dilute sulphuric acid. Add 10-15 ml 48% hydrofluoric acid to the mass. Place the crucible on asbestos sheet on a low flame or on a low temperature hot plate. Expel all acid from the crucible. Now heat the crucible initially on a low flame and finally to a blast flame ($1000^{o}C$) for about 5 minutes. Cool the crucible in a dessicator. Weigh the mass. The loss in weight will be the quality of silica. Fuse the residue in the crucible with little potassium pyrosulphate. Extract the mass in the preserved solution. Cool the filtrate and make up to 250 ml .Use this solution for the determination of major and minor elements.

Determination of CaO, MgO (EDTA Complexometry), Fe_2O_3, Al_2O_3

Follow the procedure given under the chapter on determination of major and minor constituent from the stock solution.

Determination of Na_2O, K_2O by Flame Photometry

Weigh 0.1 g of sample. Add 0.5 ml HCl and 50 ml of water. Boil. Cool. Transfer the contents in a 100 ml volumetric flask. Add ammonium carbonate and ammonia. Allow to stand for sometime. Feed this filtrate in the flame photometer and determine concentrations of Na_2O ,K_2O as given in analysis of sodium and potassium in water , waste water effluent solids soils etc.

Determination of Boron

Reagents

1. **Sodium Hydroxide Solution (0.1N):** Dissolve 40.0 gm NaOH in distilled water and dilute to 1000 ml
2. **Mannitol**
3. **Phenolphthalein solution:** 0.1 % solution in methanol or in distilled water
4. **Methyl Orange Solution:** 0.1 % solution in distilled water

Procedure

Weigh 0.1 g of sample. Add 0.5 ml HCl and 100 ml water in a 250 ml in a beaker. Boil. Cool adjust the pH to 5.2 preferably by pH meter or using methyl orange indicator solution. Add 2-3 g of mannitol and titrate with sodium hydroxide using phenolphthalein as indicator. Color changes from colorless to light pink.

1ml 1N NaOH = 0.03480 g B_2O_3

Addenda 2

LOSS ON IGNITION

Some Special Cases of Loss on Ignition

Loss on ignition of a mineral sample is very important parameter. It approximately indicates the quality and quantity of minerals present. Differential thermal analysis is totally based on thermal behavior of minerals. The data obtained can be used to estimate the quantity of the mineral. In certain samples, loss on ignition is not so simple and the sample gains the gases, especially oxygen from the atmosphere and here loss obtained needs correction. Such special cases are dealt hereunder.

1. Iron Ore

Ferrous iron present in iron ore, especially Magnetite, is oxidized during the process of loss on ignition. Many a time weight after ignition is higher than the initial weight. Here needs a correction of gain of oxygen to get correct loss of ignition.

a. Procedure

Weigh 1 g of dried iron ore (at 105^0 C) sample in a preweighed platinum crucible. Place the crucible in a muffle furnace and heat this at 300^0 C for 30 minutes. Now raise the temperature to 1000^0 C and heat the crucible for 30 minutes. Find the apparent loss or gain. Keep the ignited mass in dessicator for further analysis.

b. Correction for Ferrous Iron

Determine the ferrous iron on originally dried sample and on the residue obtained after loss on ignition as per procedure given under iron ore. Reduction in quantity of ferrous iron will indicate the gain of oxygen. Find the gain of oxygen. Correct the loss of ignition obtained above by this gain of oxygen. The final quantity is true loss of oxygen.

2 Manganese Ore

Manganese dioxide when heated loses oxygen very slowly. Manganese dioxide is converted to manganous oxide when heated at 700 ^{0} C for about 23 hour. Therefore the determination of loss of ignition is a tedious job and also to estimate the loss of ignition from other species present in manganese ore is not possible. A procedure given below can overcome the difficulty.

1. Procedure

Find loss on ignition as detailed in 1 (a) above. Store the ignited mass for further analysis.

b. Correction for Manganous Oxide

(A) Weigh 0.5 g powdered sample in a 250 ml glass beaker. Add 100 ml of 10% (w/w) sulphuric acid to this. Boil this for 10 minutes on a low flame. Cool this and filter through What man No.40.Wash the residue with acidulated (H_2SO_4) hot water. Make up the filterate to 250 ml.

Take 25 ml aliquot in a conical flask and determine manganese by Volhards method.

(B) Determine manganese on the ignited sample in the similar manner. Find the loss of oxygen by manganese dioxide from above 'A' and 'B'. Correct the loss of ignition obtained above in 2 (a) above. This value will correspond to loss of ignition to the other species present in manganese ore.

3. **Sulphide Ores**

Sulphide ore when heated sulphur from sulphide and pyrite is lost as either sulphur dioxide or the species are converted into their respective sulphates (Sulpahting roasting) This gain of oxygen due to conversion to sulphate need be used for obtaining trace value of loss of ignition.

Procedure

Weigh 1 g of dried sulphide sample in pre ignited and preweighed silica crucible (do not use platinum crucible). Place the crucible in cold muffle furnace, now raise temperature to 300^0 C. Keep this temperature for 30 minutes. Now further raise the temperature to 900^0 C and heat the crucible for 30 minutes. Cool, the crucible in a dessicator and weigh. Find the apparent loss. Keep the ignited mass in a dessicator for further analysis.

Determination of Sulphate

2. Weigh about 0.5 g sample in 250 ml glass beaker. Add 50 ml dilute hydrochloric (1:1) acid. Heat this on hot plate for about 30 minutes. Now add 50 ml oxygen free distilled water to this. Boil this on a burner to expel hydrogen sulphide gas. Cool this and filter through Whatman 40.Wash the residue with hot water.

b. Take the filterate in 600 ml beaker. Add few pieces of freshly cut aluminum foil and boil this to reduce iron. Cool and adjust acidity with methyl red indicator .Add 5 ml excess of dil.HCl. Now add 10 ml of 10% barium chloride solution in cold condition. Allow the precipitate thus formed to stand for overnight.

Decant the solution by siphon. No precipitate should pass during this process. Filter the precipitate through Whatman 42.Wash the precipitate 8-10 times with cold water. Ignite the precipitate initially at 600^0 C and finally at 800^0 C. Find quantity of SO_4.

c. Determination of SO_4 on ignited sample

Determine the quantity of SO_4 on the residue obtained after ignition as detailed under 3(a) and 9(b).

Correction for oxygen gained during sulphate formation

Find gain of oxygen from the difference of sulphate determination under 3(c) and 3 (b).Correct the loss on ignition obtained under Procedure for sulphide ores

Addenda 3

Determination of Total Silica in Silicate Mineral (A combination of Gravimetric and Photometric Method)

The precision of the photometric determination of silica is controlled to a large extent by the limitations inherent in spectrophotometry. Such determinations cannot by their nature be as precise as those obtained by good gravimetric methods, although of course the possibility of systematic errors exists in both methods. In order to combine the advantages and avoid some of the disadvantages of both methods Jeffery and Wilson have suggested a new procedure based upon a single dehydration with hydrochloric acid, giving a major silica fraction as an insoluble residue and a minor fraction the filtrate that can be determined photometrically. As only one dehydration is made, this procedure is more rapid than the classical method and as all the silica not collected in the residue is determined photometrically, it is also more accurate. Moreover, since the photometric determination is now or a minor constituent (2-8mg, equivalent to less than 1 per cent of the rock composition) the limiting accuracy of photometric methods is no longer restrictive.

A disadvantage that has been introduced is that in the filtrate from the collection of the major silica fraction, all the remaining elements have been increased in concentration relative to silica. Under these circumstance elements that are not usually present in amounts sufficient to interfere may be concentrated up to and beyond this point. Interference has been noted from titanium and phosphorus, although up to 5% TiO_2 in the rock material does not have a significant effect and upto 10% P_2O_5 can also be tolerated.

Fluorine in trace amounts does not interfere, although if present in major amounts, some of the silica may be lost by volatilization during the dehydration stage, as in the classical method for determining silicon. Three per cent fluorine in the rock material is likely to give rise to a loss of as much as 0.5% silica.

Method

Reagents

1. **Ammonium molybdate solution** Dissolve 10g of crushed ammonium molybdate in N aqueous ammonia and dilute to 10ml with N ammonia.

2. **Oxalic acid solution** Dissolve 10 g in water and dilute to 100 ml.

3. **Reducing solution** Dissolve 0.15g of 1-amino-2-naphthol-4-sulphonic acid, 0.7g of anhydrous sodium sulphite and 9 g of sodium metabisulphite in 100 ml of water. Prepare freshly each month.

4. **Standard silica stock solution** Fuse 0.20 g of pure crushed and dried crystal quartz with 1 g of anhydrous sodium carbonate in a platinum crucible.

Dissolve in water and dilute to 1 litre. This solution contains 200 µg silica per ml. Dilute with water to give a solution containing 20 µg per ml as required.

Procedure

Fuse 1 g of rock material with 5 g of anhydrous sodium carbonate in a platinum crucible and digest the melt with water. Acidify with concentrated hydrochloric acid, adding approximately 10ml in excess and evaporate to dryness in a large platinum dish. When completely dry add a further 10 ml of concentrated hydrochloric acid and sufficient water to dissolve all soluble material. Collect the silica residue on a filter, wash well with hot water and determine the major silica by hydro-fluorisation. Collect the filtrate and washings from the silica residue in a 250ml volumetric flask and dilute to volume with water.

Using a pipette, transfer 5ml of this solution to a 100ml volumetric flask and add 10 ml of water. Now add 1ml of ammonium molybdate solution and set aside for 10 minutes to complete the formation of the silicomolybdate complex. After exactly 10 minutes, add 5 ml of the oxalic acid solution, gently swirl the flask to mix the contents, and then add 2 ml of the reducing solution. The addition of the reducing solution should not be delayed. Dilute the solution to volume with water and set aside for at least 30 minutes, but preferably for 1 hour, and then measure the optical density of the solution in 2-cm cells with the spectrophotometer set at a wavelength of 650 nm.

Calibration

Transfer aliquots of the standard silicate solution containing 0-200 µg of silica to separate 100 ml volumetric flasks, dilute to 15ml with water and add 1 ml of 3 N hydrochloric acid to each. Now add 1 ml of ammonium molybdate solution to each, allow to stand for 10 minutes and then reduce the silicomolybdate to molybdenum blue as described above. Dilute each solution to volume with water and measure the optical density in 2-cm cells with the spectrophotometer set at a wavelength of 650 nm. Plot the relation of optical density to silica concentration. As the calibration graph is a straight line passing through the origin, a single point method can be used for subsequent calibrations.