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*Draft Indian Standard*

**Methods of Chemical Analysis of Iron Ores**  
**Part 1 Determination of Common Constituents**

[Second Revision of 1493 (Part 1)]

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Method of Chemical Analysis of Metals  
Sectional Committee, MTD 34

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**NATIONAL FOREWORD**

Since the publication of this standard, several ISO standards on the elemental determination of common constituents given in the standard have been published. These determinations need to be harmonized with the corresponding ISO standards so as to specify the acceptance of analytical values based on the permissible tolerance between and within laboratories.

In order to take care of the various factors involved in the procedures, the existing IS Standard has been changed as:

- a) A general clause has been added detailing the guidelines for factors involved.
- b) Wherever required, the procedures of determinations have been suitably altered, incorporating the repeatability or reproducibility of the elemental analytical values as per the ISO standards.
- c) Inclusion of the method of calculation of total Iron on the natural, as received basis as a new item as per commercial requirement.
- d) The procedure for the determination of Sulphur is modified to eliminate the use of MIBK instead of pure Aluminium metal powder has been used to reduce ferric iron to ferrous iron presence of which does not interfere with the accuracy of the method.
- e) The method of determination of Acid Soluble Iron as per ISO 9035:1989 'Iron ores – Determination of acid-soluble iron (II) content – Titrimetric method' as it is, included in this revision.
- f) The method of determination of total iron content-titrimetric methods after titanium (III) chloride reduction as per ISO 2597-2:2019 included in this revision.

For the purpose of deciding whether particular requirement of this standard is complied with the final value, observed or calculated, expressing the result of a test or analysis, shall be rounded off in accordance with IS 2: 1960 'Rules for rounding off numerical values (*revised*)'. The number of significant places retained in the rounded off value should be the same as that of the specified value in this standard.

## 1 SCOPE

This standard prescribes method of determination of moisture, Silica, Total Iron, Acid Soluble Iron, Aluminum, Phosphorous (for > 0.015 percent) and Sulphur in Iron Ores, natural and processed, concentrates and agglomerates, such as pellets and sinters.

## 2 REFERENCES

The following standards contain provisions, which through reference in this text, constitute provisions of this standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreement based on this standard are encouraged to investigate the possibility the applying the most recent editions of the standards indicated below:

<i>IS No.</i>	<i>Title</i>
1070:1992	Reagent grade water ( <i>third revision</i> )
1405:2010	Methods of sampling of iron ores ( <i>third revision</i> )
7659(Pt 1):1975	Reagent and standard solutions for use in chemical analysis of metals, ores and minerals Part 1 volumetric solution
8167:1989	Method for determination of reducibility index of iron ore oxides, lumps core, sinter and pellets ( <i>first revision</i> )
11292:1985	Determination of relative reducibility of iron oxides; lump ore, sinter and pellets
11607:1986	Method of sampling of Iron Ore Sintors
9101:1979	Method of sampling of Iron Ore Pellets
11690: 1986	Methods of moisture determination of iron ore lot
264: 2005	Nitric Acid ( <i>third revision</i> )
265: 1993	Hydrochloric Acid ( <i>fourth revision</i> )
460 (Part-1): 2020	Test Sieves (wire cloth test sieves) ( <i>fourth revision</i> )

## 3 SAMPLING

**3.1** Samples for the purpose of chemical analysis shall be drawn and prepared in accordance with IS 1405, IS 9101 and IS 11607.

### 3.2 Preparation of Sample

**3.2.1 Moisture Samples** – The sample prepared especially for the purpose of moisture determination and preserved in an air-tight container shall be used. The contents of the container shall be emptied on a non-absorbent paper like wax paper, mixed thoroughly by rolling and spread uniformly. From this a representative sample taken from all sided with a spatula shall constitute the moisture sample. The moisture sample, however, shall not be used for the purpose of chemical analysis even after further crushing.

\*Method of chemical analysis of iron ores.

†Rules for rounding off numerical values (revised).

**3.2.2 Samples for Chemical Analysis** – The laboratory sample prepared for the purpose of chemical analysis (*see* IS 1405) shall be pulverized preferably to pass through 150 micron standard sieve (*see* IS 460 part-1). The pulverized sample shall be mixed thoroughly by rolling on a non-absorbent paper and spread uniformly. From this a sufficient quantity shall be taken as representative sample and transferred to glass or stainless steel Petri dish, ground to –150 micron,

closed with a cover and dried in a hot air oven at  $105 \pm 5^{\circ}\text{C}$  for about 2 hours or more and then cooled in desiccator (containing Calcium chloride, calcined at 700 to  $800^{\circ}\text{C}$ ). This dried sample shall be used for the purpose of chemical analysis, and is termed as a test portion.

For ores, which are known to be of hygroscopic nature, the sample (ground to -150 microns) shall be analyzed on as received basis and the results reported on dry basis (*i.e* dried at  $105 \pm 5^{\circ}\text{C}$ ). For this purpose, the hygroscopic moisture shall be determined simultaneously with the analysis and correction factor found out as follows, shall be applied for each determination for reporting on dry basis.

Dry a glass Petridish with cover in an air oven at  $105 \pm 5^{\circ}\text{C}$ , cool in a desiccators and weigh. Weigh approx. 5 g (m) of the ground sample (-150 micron size), and transfer it to the Petri dish. Close the cover and heat it in the air oven at  $105 \pm 5^{\circ}\text{C}$  to a constant mass (nearly 2 hrs of drying may be enough), cool in a desiccator and weigh. From the loss in mass, calculate the correction factor (*k*) as follows (correct to four places of decimals) all weights shall be recorded to nearest 0.1 mg.

$$k = \frac{100}{100-A}$$
$$A = \frac{(m_2-m_1)}{m} \times 100$$

Where

$m_1$ =mass in g of the empty Petri dish with cover (dried)

$K$  =correction factor

$m_2$ =mass in g of the Petri dish with sample and cover after drying; and

$A$  = *Percentage* hygroscopic moisture

$m$  = Actual weight of sample

## 4 TERMINOLOGY

- 4.1 Precision: Closeness of agreement between mutually independent test results obtained under prescribed conditions of the test procedure.
- 4.2 Independent test result: Results obtained in a manner not influenced by any previous results on the identical test sample, within a short interval of time.
- 4.3 Permissible tolerance within-laboratory-expressed by symbol 'r' (also termed repeatability): Critical value, which the absolute difference between two independent test results, obtained in the same laboratory, by the same analyst, using the same test method and same equipment on identical test sample, within a short interval of time, expected to be less than or equal to, with a prescribed probability of 95 percent.

## 5 GENERAL

## **5.1 APPARATUS**

**5.1.1** Weighing shall be carried out using an analytical balance with a constant sensitivity. It shall be capable of weighing 200 g maximum, and shall be able to read a difference of 0.1 mg

**5.1.2** The weighing devices (balances and weights) and laboratory measuring glass equipment's (burettes, pipettes, volumetric flasks, and measuring cylinders) shall be of certified quality and shall be verified for calibration and appropriate corrections shall be applied, from time to time.

**5.2 Filter paper:** The filter paper of medium texture, with low ash content.

## **5.3 Number of Test Portions**

To determine the content of a particular element at least independent duplicate analysis shall be carried out simultaneously. The arithmetic mean of the duplicate values shall be reported however, the range of the values obtained shall not exceed the limits of permissible tolerance, wherever specified under each elemental analytical procedure. If the range of the value falls outside the limit of permissible tolerance, the cause for this deviation shall be ascertained and determination shall be repeated on fresh samples as indicated in Annex-A.

## **5.4 Blank Test**

Parallel with the determination and under the same conditions, blank test on the reagents shall be carried out and appropriate correction shall be applied to the result of the determination.

## **5.5 Check test**

Parallel with the determination and under the same conditions a check analysis shall be carried out on a standard certified sample of iron ore (standard reference material, SRM) having approximately the same concentration of the element under analysis, and based on the certified value of the final result of the element under chemical analysis.

In order to maintain the precision and accuracy of the analytical values of the element, strict adherence to the standard procedure, detailed under each elemental analysis, shall be ascertained.

## **5.6 Expression of the Analytical Values**

The analysis values shall be expressed in mass, percent of the weighed out of the dried sample and rounded to the minimum place of the decimals as specified below:

- a) Elements to be expressed to two places of decimals: Total iron, Silica, Aluminum and Acid soluble iron.
- b) Elements to be expressed to three places of decimals: Phosphorus, Sulphur.

## **5.7 Permissible Tolerance**

The permissible Tolerance within a laboratory and between two laboratories are to be indicated for each elemental determination.

**5.8** A general flow sheet of the procedure of the acceptance of the analytical values for elemental determination is given in Annex A.

### **5.9 Test Report**

The final test report shall include the following information:

- a) Identification of the sample in detail, including the reference number of the report, the laboratory and date of analysis.
- b) Reference to the Indian standard for method of analysis.
- c) Any other characteristics noticed during the determination and any Operations not specified in the relevant Indian Standard, which may have an influence on the analytical results.

## **6. Reagents**

**6.1** All reagents used shall be pure chemicals of (A.R.) analytical reagents grade, which do not contain impurities, which would affect the analytical results.

**6.2** Distilled water (*see* IS 1070) or de-ionized water shall be used in the preparation of the reagents and throughout the analysis.

**6.3** All solutions shall be freshly prepared. The method of preparation of standard solutions shall be in accordance with IS 7659 (Part 1).

**6.4** Reagents, which are poisonous, shall be properly labeled and shall be allowed to be handled by the authorized chemists with proper instructions. The concentrations of solutions are often expressed in the following form, if not expressed otherwise.

- a) “Percent ( $m/v$ ) or ( $w/v$ )”, meaning the mass in grams of the component in 100 milliliters of solution.
- b) “percent ( $m/m$ ) or ( $w/w$ )”, meaning the mass in grams of the component in 100 g of solution.
- c) “1: 4 ( $v/v$ )”, meaning mixing of one part (first figure) by volume of the component with four parts (second figures) by volume of the solvent.

## **7 DETERMINATION OF MOISTURE IN MOISTURE SAMPLE**

**7.1 Procedure** – Dry a glass or preferably aluminum petri dish in an oven at 105<sup>0</sup> C to 110<sup>0</sup> C, cool in a desiccator and weigh. Transfer to this about 100 g of the well-mixed moisture sample ( *see* 3.2.1 ). Spread the sample uniformly in the dish and weigh. Dry the sample in an oven at 105<sup>0</sup> C to 110<sup>0</sup> C to constant weight. It is recommended that weight is taken after three hours of drying and subsequent cooling in a desiccator. Thereafter, drying is continued and weight taken after every hour of drying until the weight remains constant. In practice it is found that, after all the moisture has been expelled by drying, the weight increases slightly due to oxidation. In such a case, the lowest weight reached is used for calculating the total moisture.

$$\text{Moisture, Percent} = \frac{\text{Loss of mass in g}}{\text{Mass in g of sample taken}} \times 100$$

## **8 DETERMINATION OF SILICA BY GRAVIMETRIC METHOD AND PREPARATION OF THE MAIN SOLUTION (Applicable for Silica between $\geq 0.5$ percent).**

### **8.1 Outline of the Method**

The sample is dissolved in hydrochloric acid, and baked for dehydration of silica which is filtered and determined by volatilization with hydrofluoric acid. The insoluble residue is fused with sodium carbonate, extracted with hydrochloric acid and added to the main filtrate obtained on the first filtration. The solution is made up to a definite volume and reserved for further analysis. (Main solution)

### **8.2 Reagents**

- 8.2.1 Concentrated Hydrochloric Acid – rd = 1.16 (conforming to IS 265)
- 8.2.2 Concentrated Nitric Acid – rd = 1.42 (conforming to IS 264)
- 8.2.3 Dilute Hydrochloric Acid – 1 : 1 and 1:20 (v/v)
- 8.2.4 Dilute Sulphuric Acid – 1 : 1 and 1.20 (v/v)
- 8.2.5 Hydrofluoric Acid – 40 percent
- 8.2.6 Sodium Carbonate – Solid
- 8.2.7 Potassium Bisulphate – Solid
- 8.2.8 Perchloric Acid – rd = 1.67 (70 percent m/m)

### **8.3 Procedure**

#### **8.3.1 Preparation of Sample for Chemical Analysis**

The necessary portion of the sample required for chemical analysis is dried in aluminum or glass petri dish at 105°C for 1.5 to 2 hrs. The dish is cooled in a desiccator and from this dried sample, the necessary portions required for different determinations are weighed.

#### **8.3.2 For ores containing Titanium Dioxide $\leq 2$ percent**

**8.3.2.1** Weighed accurately 2.000 g of the sample and transfer it to a 400 ml beaker. Add 35-40 ml of concentrated hydrochloric acid and 5 to 10 drops of concentrated nitric acid. Cover the watch-glass and digest on a hot plate. Avoid boiling and stir the contents gently and occasionally. Continue digestion until all the ore is attacked and no black particles are left. Remove the watch-glass and wash with a little water.

**8.3.2.2** Evaporate the contents to dryness on low heat and bake the residue at about 120°C (low in hot plate) for 1 hr. Cool somewhat and take up the residue in 10 ml of concentrated hydrochloric acid and dilute to about 20 ml. Warm the solution for dissolution (at 70-

80°C) of the dried mass under cover. Filter (6.2) the solution through filter paper and transfer all the insoluble matter from the beaker to filter paper using a policeman or rubber tipped glass-rod. Receive the filtrate in a 250 ml volumetric flask. Wash the residue with hot dilute hydrochloric acid (1:20) till the filter paper is free of ferric chloride. Finally wash the residue with hot water four or five times. Preserve the filtrate (A).

**8.3.2.3** For sinters and ores having silica content in excess of 5 percent, silica should be recovered from filtrate (A) as follow:

Add 10 ml of perchloric acid and 1 ml of sulphuric acid to the filtrate (A) and heat until dense white fumes of perchloric acid appear. Cover the beaker completely and continue heating until there are no more fumes in the beaker and most of the perchloric acid has evaporated. Avoid evaporation to dryness. Allow to cool, add 25 ml hydrochloric acid and gently heat to dissolve the soluble salts. Add about 30 ml water mix and collect the residue, quantitatively on the same filter paper on which insoluble matter is collected.

**8.3.2.4** Ignite the residue in a platinum crucible in a muffle furnace raising the temperature of the furnace slowly at the beginning and then maintaining the furnace at 1050°C for about 30 minutes. Cool the residue in the platinum in the platinum crucible in a desiccator and weigh. Moisten the residue with a little water and a few drops of dilute sulphuric acid (1 : 1) and 8 to 10 ml of hydrofluoric acid. Evaporate to dryness and repeat the procedure adding about 5 ml of hydrofluoric acid and weigh platinum crucible. Calculate the percentage of silica **(8.5)**

**8.3.2.5** After determination of silica, fuse the residue left in the crucible with about 1 g of sodium carbonate. Extract the fused mass with dilute hydrochloric acid (1 : 1) and preserve the filtrate (B).

**8.3.3** *For Ores Containing Titanium Dioxide  $\geq 2$  Percent.*

**8.3.3.1** Weigh accurately 2.000 g of the sample and dissolve in concentrated hydrochloric acid as given in 8.3.2.1. Add to the solution, 40 ml of dilute Sulphuric acid (1:1). Evaporate the contents on a hotplate or sand-bath until copious fumes of Sulphuric acid are evolved. Cool thoroughly and dissolve the residue in 100 ml water by boiling. Filter (6.2) the solution and transfer the residue adhering to the beaker by means of rubber-tipped glass-rod. Wash the residue 7 to 8 times with hot dilute sulphuric acid. Preserve the filtrate (A).

**8.3.3.2** Dry and ignite the residue in a platinum crucible until all the carbon is burnt off. Cool and fuse the residue with 2 to 3 g of Potassium bisulphate for about 5 minutes. Cool and extract the fused mass in a 400 ml beaker containing about 75 ml water and 25 ml of dilute sulphuric acid (1:1). Wash the crucible and lid into the beaker. Evaporate the solution carefully and heat until copious fumes of sulphuric acid are evolved. Cool thoroughly and dissolve the residue in about 100 ml water by boiling until all the soluble portion is dissolved. Filter (6.2) the solution and transfer the residue adhering to the beaker by means of a rubber-tipped glass rod. Wash the residue 7 to 8 times with hot dilute sulphuric acid (1 : 20). Preserve the filtrate (B). Treat the residue as directed in 8.3.2.4. The recovery of soluble silica in a filtrate (B) shall be as per 8.3.2.3.

**8.3.3.3** After the silica has been volatilized by treatment with hydrofluoric acid, fuse the residue in the platinum crucible with about 1 g of Potassium bisulphate for about 5 minutes. Extract the fused mass in 60 to 70 ml of hot dilute sulphuric acid (1 : 20). Wash the crucible and lid into the same beaker. Preserve the solution (C).

**8.4 Preparation of main solution** – Combine the filtrate (A) and obtained in 8.3.3.1 or 8.3.2.2 with the filtrate (B) obtained in 8.3.2.5 or 8.3.3.2 and the solution (C) obtained in 8.3.3.3 in the case of titanium ferrous ores. Concentrate, if necessary, and transfer to a 250 ml volumetric flask, cool and make up to the mark and mix well. This is the solution of 2.000 g of the sample free from silica, which is hereafter referred to as the main solution. From this solution, the determination of iron, and aluminium may be carried out.

## 8.5 Calculation

$$\text{Silica, present} = \frac{(A-B)}{C} \times 100$$

Where

A = mass of the crucible including residue before hydrofluorization;

B = mass of the crucible including residue after hydrofluorization; and

C = mass of the sample taken.

**8.5.1** Calculate the Silica content to four decimals places. Carry out independent duplicate analysis. The final result shall be reported to two decimal places, based on the directions given in clause 8.4

## 8.6 Repeatability (r) and Permissible Tolerance (R)

The repeatability within a laboratory (r) of the silicon content is expressed by the following regression equation based on the arithmetic mean of the two independent duplicate values Si percent.

$$r = 0.0511 + 0.0090 \times \text{Si \%}$$

The permissible tolerance between the laboratories (R) of the silicon content, based on the arithmetic mean of the final results reported by the two laboratories Si percent is expressed by the following regression equation.

$$R = 0.0831 + 0.0095 \times \text{Si \%}$$

The agreement of the final results reported by the two laboratories shall be decided according of **4.3**

## 8.7 Si Factor

$$\text{Si} = \text{SiO}_2 \times 0.4672$$

## 9. DETERMINATION OF TOTAL IRON

**9.1** Trivalent Iron is reduced, using stannous chloride, to ferrous state and the reduced iron, is titrated with standard potassium dichromate solution (after oxidation of the excess reductant with mercuric chloride).

**9.1.1** The method is applicable to total iron content between 30 and 72 percent however the total iron contents from 1 percent to 30 percent can also be determined.

**9.1.2** The suggested procedure for the removal of the mercury from the waste solutions before discharge to effluent drains is given in **Annex B**.

**9.1.3** The determination of Total Iron content, if required to be reported, on natural, as received basis, it shall be carried out as per clause **9.8**

## **9.2 Reagents**

**9.2.1** Concentrated Nitric Acid – rd 1.42

**9.2.2** Ammonium Chloride – solid

**9.2.3** Ammonium Hydroxide — rd 0.89

**9.2.4** Methyl Red Indicator — 0.5 percent in distilled water.

**9.2.5** Ammonium Chloride wash liquid (5 percent) — Ammonium Chloride solution neutralized with Ammonium Hydroxide using Methyl Red indicator.

**9.2.6** Concentrated Hydrochloric Acid – rd 1.16

**9.2.7** Dilute Hydrochloric Acid — 1 : 4 (v/v), 1 : 1 (v/v) 1N and 6N.

**9.2.8** Di-phenylamine Sulphonate Indicator Solution — Dissolve 0.2 g of powdered sodium di-phenylamine sulphonate in a small volume of water and dilute to 100 ml. Store this solution in a brown glass bottle.

**9.2.9** Standard Potassium Dichromate Solution (0.1N) — Weigh exactly 4.903 g of potassium dichromate [minimum purity 99.9 percent (m/m)] and dissolve in water in 1 000 ml volumetric flask and make up the volume up to the mark. Mix thoroughly. Record the temperature ( $t_1$ ) at which this dilution is made. The solid reagent shall be dried at 140°C in the air bath for 2 hour and cooled in a desiccator before weighing.

$$1 \text{ ml } 1\text{N } \text{K}_2\text{Cr}_2\text{O}_7 = 0.05585 \text{ g (Fe)}$$

**NOTE** — This being a primary standard the solution may not be standardized and the purity indicated in the standard reagent shall be used as a factor to N/10 as it is; however in case the purity is lower than the stipulated, it shall be standardized using a standard reference material of nearly the same Iron content

### **9.2.10 Stannous Chloride Solution**

Dissolve by heating 60 g of pure stannous chloride in a mixture of 400 ml of concentrated hydrochloric acid and 600 ml of water until dissolution is complete. Cool and add a few pieces of granulated tin and preserve the solution in an air-tight amber coloured bottle to prevent oxidation.

### **9.2.11 Mercuric Chloride Solution**

Prepare a Saturated solution of mercuric chloride in water.

### **9.2.12 Sulphuric Acid – Phosphoric Acid Mixture**

Add slowly 150 ml of concentrated sulphuric acid to 700 ml of water with continuous stirring. Add to this 150 ml of syrupy phosphoric acid. Destroy any oxidizable impurities by adding potassium permanganate solution ( 0.1 N) drop by drop until the pink colour of permanganate persists, and cool the solution.

### **9.2.13 Iron Standard Solution**

Weigh, to the nearest 0.002 g, 5.58 g pure Iron [minimum purity 99.9 percent (m/m)] into a 500 ml conical flask and place a small filter funnel in the neck. Add 75 ml hydrochloric acid (1 : 1 v/v) in small increments and heat until the Iron is dissolved. Cool and oxidize with 5 ml of Hydrogen Peroxide [30 percent (m/m)] added in small portions. Heat to boiling and boil to decompose the excess hydrogen peroxide to remove chlorine. Transfer to a 1000 ml volumetric flask (one-mark), dilute to volume with water and mix. 1 ml of this solution is equivalent to 1 ml of potassium dichromate standard volumetric solution.

### **9.2.14 Dilute Phosphoric Acid — 1 : 1 ( v/v ).**

### **9.2.15 Concentrated Perchloric acid- rd 1.7**

### **9.2.16 Titanium(III) chloride (TiCl<sub>3</sub>) solution, 20 g/l, dilute one volume of titanium chloride solution (about 20 % TiCl<sub>3</sub>) with nine volumes of 1:1 hydrochloric acid.**

Alternatively, dissolve 1.3 g of titanium sponge in about 40 ml of concentrate hydrochloric acid in a covered beaker by heating in a water bath. Cool the solution and dilute with water to 200 ml. Prepare fresh solution as needed

### **9.2.17 Dilute Potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) solution, 1 g/l.**

### **9.2.18 Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), 30 % by volume solution.**

### **9.2.19 Dilute Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), 30 % by volume solution, diluted 1: 9**

### **9.2.20 Potassium permanganate (KMnO<sub>4</sub>) solution, 25 g/l.**

### **9.2.21 Dilute Sulfuric acid 1:1 (v/v)**

### **9.2.22 Indigo carmine [5.5'-disulfonic acid disodium salt (C<sub>16</sub>H<sub>8</sub>O<sub>8</sub>N<sub>2</sub>S<sub>2</sub>Na<sub>2</sub>)] solution, 0.1 g/100 ml, dissolve 0.1 g of indigo carmine in a cold mixture of 50 ml sulfuric acid (9.2.21) and 50 ml of water**

## **9.3 Procedure (by Stannous Chloride Method)**

**9.3.1** Pipette out 50 ml. of the main solution in 400 ml beaker dilute to 150 ml volume and add about 3 g of ammonium chloride. Boil and precipitate R<sub>2</sub>O<sub>3</sub> by dropwise addition of ammonium hydroxide. Dissolve the R<sub>2</sub>O<sub>3</sub> in 20 to 25 ml. of dilute hydrochloric acid (6N) and transfer the solution to a 500 ml. conical flask. Wash the beaker with a little water

and transfer the washings to the conical flask. Heat to boiling for a while and add stannous chloride solution drop wise to the boiling solution with constant swirling until the yellow colour solution becomes just colourless. Add 2-3 drops excess stannous chloride solution and wash the sides with water. Cool the flask rapidly under running tap water or otherwise until the contents have cooled down to room temperature.

**9.3.2** Add about 10 ml of mercuric chloride solution and shake the flask. At this stage, a silky white precipitate appears. Wait for about 2 minutes, dilute to 150 to 170 ml. volume and add 15 ml of sulphuric acid- phosphoric acid mixture. Add 3 to 4 drops of diphenylamine sulphonate indicator solution and titrate with standard potassium dichromate solution continuously until a stable violet blue colour persists. Record this volume as  $V_1$  ml.

#### **9.4 Procedure (By Silver Reductor Methods) (Alternative Method)**

**9.4.1** Pipette out an aliquot equivalent to 0.4g (50 ml) from the main solution in a 400-ml beaker. Add about 1 ml of concentrated nitric acid and boil the solution for about 5 min. Cool somewhat, dilute to 150 ml volume and add about 3 g of ammonium chloride. Boil again and re-precipitate  $R_2O_3$  by dropwise addition of ammonium hydroxide adding methyl red indicator towards the end. Boil for a while for better coagulation and allow the precipitate to settle.

**9.4.2** Filter hot through filter paper (6.2) and wash the residue 5 or 6 times with hot ammonium chloride wash liquid. Transfer back the precipitate to the original beaker, wash the filter paper with hot dilute hydrochloric acid (1:4) and collect the washings into the beaker.

**9.4.3** Dissolve the residue in the beaker with 10 ml of hot dilute hydrochloric acid (1:1) and 30-40 ml of water. Adjust the acid strength of the solution to about 1 N dilute hydrochloric acid by adding water. Cool the solution into room temperature and pass through silver reductor at the rate of 25-30 ml per minute as given in Annexure-C. Collect the solution passing through the reductor in a 400-ml beaker. Wash the beaker and the reductor thoroughly with hydrochloric acid wash liquid ( 1 N ). ( Six washings of about 20 ml volume in each washing are sufficient. ). After collecting the washings, add 5 ml of dilute phosphoric acid and 5 or 6 drops of diphenylamine sulphonate indicator solution. Stir to mix properly and titrate with standard potassium dichromate solution till the violet blue colour persists.

#### **9.5 Procedure (Titrimetric methods after titanium(III) chloride reduction) (Alternative Method )**

**9.5.1** Method 1: Oxidation of excess titanium (III) chloride with dilute dichromate solution using indigo carmine indicator solution

Pipette out 50 ml. of the main solution in 400 ml beaker and heat at 90 °C to 95 °C and wash the cover and inside wall of the beaker in a small amount of hot water. Immediately add stannous chloride solution dropwise to reduce iron (III), while swirling the solution in the beaker until only a faint yellow tint of the iron (III) chloride solution remains.

It is essential that some iron(III) remain unreduced. If the solution is made colourless by the excessive addition of stannous chloride solution, add hydrogen peroxide or potassium permanganate solution dropwise until the solution changes to a faint yellow tint.

NOTE It is convenient to use dilute potassium dichromate solution as a reference solution for establishing the desired slight yellow tint of the iron solution. The solution is prepared by diluting 5 ml of potassium dichromate standard solution to 100 ml with water.

Wash the inside wall of the beaker using a small amount of hot water. Add 3 to 4 drops of indigo carmine solution as indicator, then titanium(III) chloride solution drop by drop, while swirling the solution, until it turns blue, then colourless. Add 2 to 3 drops in excess. Immediately add dilute potassium dichromate solution drop by drop, to oxidize the excess of titanium (III) chloride, until the solution changes to a persistent blue colour which lasts for 5 s.

Place in a cooling bath for several minutes, then dilute the solution to about 300 ml using cold water. Follow the procedure specified in 9.5.3

#### **9.5.2 Method 2: Oxidation of excess titanium (III) chloride solution with perchloric acid**

Pipette out 50 ml. of the main solution in 400 ml beaker and heat at 90 °C to 95 °C and wash the cover and inside wall of the beaker with a small amount of hot water. Immediately add stannous chloride solution dropwise to reduce iron(III), while swirling the solution in the beaker until only a light-yellow colour remains (see NOTE in 9.5.1).

Reduce the remaining iron(III) by adding titanium(III) chloride solution, drop by drop, until the yellow colour has disappeared, then add an additional 3 to 5 drops. Wash the inside wall of the beaker with a small amount of water and reheat rapidly to an incipient boil. Remove from the source of heat and immediately add, all at once, 5 ml of perchloric acid. Mix well by swirling for about 5 s. Dilute immediately with cold (< 10 °C) water to 300 ml. Cool rapidly to < 15 °C and follow the procedure specified in 9.5.3

#### **9.5.3 Titration**

Titrate the cold solution obtained in accordance with 9.5.1 or 9.5.2 with the potassium dichromate standard solution, while swirling, until the amount of the titrate reaches 10 ml. Add 30 ml of sulfuric acid-orthophosphoric acid mixture and continue to titrate with the potassium dichromate standard solution using 3 to 4 drops of the sodium diphenylaminesulfonate solution as an indicator. The end point is reached when the green colour of the solution changes to a bluish green and a final drop of the titrant imparts a violet colour. Record this volume as  $V_1$  ml.

NOTE Barium diphenylaminesulfonate can be used as an indicator.

The ambient temperature of the potassium dichromate solution should be noted. If this differs by more than 1 °C from the temperature at which it was prepared (20 °C), make the appropriate volumetric correction: 0.02 % relative for each 1 °C of difference (for example, the titre should be decreased when the ambient temperature during the titration is higher than the temperature during preparation of the standard volumetric solution). A correction for the temperature difference, if any, is essential.

### **9.6 Blank Test**

Determine the blank test value, using the same amount of reagents and following all the steps of the procedure 9.3.1 or 9.4.1 or 9.5.1 respectively. Immediately before reduction with stannous chloride solution add exactly 1.0 ml of Iron standard solution with one-mark calibrated pipette and titrate the solution as described in 9.3.2 or 9.4.3 or 9.5.3 respectively.

Record the volume of this titration  $V_0$ .

The blank test value of this titration  $V_2$  is calculated using  $V_2 = V_0 - 1.0$

**NOTE** — In absence of Iron the diphenylamine sulphonate indicator does not react with the potassium dichromate standard solution.

## 9.7 Calculations

$$\text{Total Fe, percent} = \frac{(V_1 - V_2) [1 - (t_2 - t_1)] \times 0.0002 \times A \times 0.055847 \times 100 \times K}{B}$$

Where,

$V_1$  = Volume in ml. of the standard dichromate solution

$V_2$  = Volume in ml. of the standard dichromate solution consumed in the Blank test.

$t_1$  = temperature in degree Celsius at which the standard potassium Dichromate solution was prepared.

$t_2$  = temperature in degree Celsius at which the standard potassium dichromate solution was titrated.

$B$  = mass in grams of the sample representing the aliquot.

$A$  = normality of the standard potassium dichromate if standardized with SRM, if not use 0.1 N.

$K$  = 1, if pre dried test sample

## 9.8 Permissible Tolerance.

**9.8.1** Permissible tolerance of the independent duplicate results within the same Laboratory (repeatability),  $r = 0.235$ .

**9.8.2** Permissible tolerance limit between the results of the two laboratories  $R = 0.530$ .

## 9.9 Calculation of the Final Iron Content.

The final results shall be obtained as the arithmetic mean of the analytical values of the samples as determined by the operations specified in Annexure A, calculated to the fourth decimal place and rounded off to the second decimal place.

## 9.10 Determination of Total Iron Content on Natural (as received) basis, of a lot or sub-lot of Iron ore.

$$= \frac{(100 - \text{Moisture\%}) \times (\text{Total Iron\% on dry basis})}{100}$$

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Total Fe% (Natural Basis)	100
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Where:

Total Iron% is that obtained from 9.7 of lot or sub-lot and moisture% is the moisture of the lot or sub-lot of the Iron ore determined according to IS 11690.

### 9.11 Oxide Factors

$$\% Fe \times 1.430 = \% Fe_2O_3$$

$$*\% Fe (II) \times 1.286 = \% FeO$$

$$\% Fe \times 1.382 = \% Fe_3O_4$$

\* Fe (II) is acid soluble iron content

## **10 DETERMINATION OF ACID-SOLUBLE IRON Fe(II) CONTENT IN NATURAL AND PROCESSED IRON ORES CONTAINING FROM 0.1 TO 25 PERCENT ACID SOLUBLE IRON AND ONLY TRACES OF METALLIC IRON**

### **10.1 Outline of the Method**

Dissolution with hydrochloric acid in an inert atmosphere, addition of a mixture of sulfuric and phosphoric acid and dilution with water. Determination of the iron (II) content by titration with potassium dichromate standard solution using sodium diphenylamine sulfonate as indicator. This method is specially limited for in construction with the reducibility test methods (*see* IS 8167 and IS 11292).

### **10.2 Reagents**

**10.2.1** During the analysis use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

The water used for the procedure should be de-oxygenated by boiling.

**10.2.2** Sodium Carbonate ( $\text{Na}_2\text{CO}_3$ ) or Sodium hydrogen Carbonate ( $\text{NaHCO}_3$ )

**10.2.3** Hydrochloric Acid d 1.16 g/l or 1.19 g/l

This reagent should be de-oxygenated by purging with either nitrogen or argon, or by heating for a short time.

**10.2.4** Hydrofluoric Acid- 40 percent (m/m), d 1.13 g/l or 48 percent (m/m), d 1.16 g/l

NOTE - d represent specific gravity.

**10.2.5** Sodium carbonate or Sodium hydrogen carbonate

Saturated solution at ambient temperature.

**10.2.6** Sulfuric acid-phosphoric acid mixture

To 300 ml of water, add cautiously 150 ml of sulfuric acid (d 1.84 g/l) with constant stirring. *After cooling* add 150 ml of phosphoric acid (d 1.71 g/l). Cool and dilute with water to 1000 ml

**10.2.7** Nitrogen (99.99 percent  $\text{N}_2$ ) or argon (optional)

**10.2.8** Potassium dichromate, standard volumetric solution

( $\text{K}_2\text{Cr}_2\text{O}_7 = 0.01667 \text{ mol/l}$ )

Dissolve 4.904 gm of pulverized potassium dichromate (dried at 140°C to 150°C for 2 hours and cooled to room temperature in a desiccator) in water and dilute to a volume of 1000 ml after cooling to 20°C.

### 10.2.9 Sodium Diphenylamine Sulfonate Solution

Dissolve 0.2 g of powdered sodium diphenylamine sulfonate ( $\text{C}_6\text{H}_5\text{NHC}_6\text{H}_4\text{SO}_3\text{Na}$ ) in 100 ml of water. Store the solution in a brown glass bottle.

#### NOTES

1. Alternatively, an equivalent quantity of indicator in pellet form may be used.
2. Barium, diphenylamine sulfonate may be used instead of sodium diphenylamine sulfonate.

## 10.3 Apparatus - General laboratory apparatus

**10.3.1** Conical flask, of capacity 500 ml.

**10.3.2** Gockel safety trap or an apparatus with a feed tube for inert gas See Fig.1 and Fig. 2 (refer Annex B)

NOTE – Alternatively, a silt rubber valve (Bursen valve) may be used, but its efficiency depends on the length of the silt and the quality and the flexibility of the rubber tubing.

**10.3.3** Burette, Class B

## 10.4 Procedure

### 10.4.1 Test Portion

Taking several increments, using a non-magnetic spatula, weight to the nearest 0.002 g approximately 0.5 g of the pre-dried test sample (pulverized to minus 150 microns size ) dried at  $105 \pm 2^\circ\text{C}$ .

NOTE – The test portion should be taken and weighed quickly to avoid re-absorption of moisture. If the ore has significant content of combined water or oxidizable compounds, use particle size of minus 150 micron.

### 10.4.2 Decomposition

**10.4.2.1** Transfer the predried test portion to a dry 500 ml conical flask and 1 to 2 g of solid sodium hydrogen carbonate or sodium carbonate and 30 ml hydrochloric acid. For ores with high silica content i.e  $> 5$  percent (m/m)  $\text{SiO}_2$ , add few drops of hydrofluoric acid. Immediately close the flask with a Gockel safety trap Fig-2 which contains sodium hydrogen carbonate or sodium carbonate solution or is to be flushed with nitrogen or argon at 0.5 l/min during the decomposition. Heat the flask heating plate at a temperature of about  $90^\circ\text{C}$  until complete decomposition of the test portion.

NOTE – The decomposition time should not exceed 60 min. Normally a decomposition time of 30 min, is sufficient. In order to ensure the complete decomposition of the sample, a duplicate determination may be performed using twice the decomposition time, provided that this time does not exceed 50 min.

**10.4.2.2** When the closed flask has cooled, remove the valve and wash away the iron chlorides adhering to the stem of the valve with water.

## 10.5 Titration

**10.5.1** Add 30 ml of sulphuric acid –phosphoric acid mixture to the solution, dilute with water to about 300 ml and add about 5 to 6 drops of sodium diphenylamine sulfonate solution as an indicator. Titrate immediately with the potassium dichromate standard solution until the colour of the solution changes from green to bluish green to violet with the last drop of titrant.

NOTE – The ambient temperature of the potassium dichromate solution should be noted. If it differs by more than 2°C from the temperature at which it was prepared, make the appropriate volumetric correction; 0.025 ml relatively for each 1°C of difference. i.e. the titrate should be decreased when the ambient temperature during the titration is higher than the temperature during preparation of the standard volumetric solution.

### 10.5.2 Check Test and Blank Test

**10.5.2.1** In each run, one analysis of a certified reference material of the same type of ore shall be carried out in parallel with the analysis of the ore sample (s) under the same condition.

**10.5.2.2** When the analysis is carried out on several samples of the same type of ore at the same time, the analytical value of one certified reference material may be used.

**10.5.2.3** Carry out a blank test and subtract the blank value from the analytical value.

NOTE – The certified reference material should be of same type as the sample to be analysed and the properties of the two materials should be sufficiently similar to ensure that in either case no significant changes in the analytical procedure will become necessary.

## 10.6 Expression of Results

### 10.6.1 Calculation of Acid Soluble Iron Content Fe (II)

The iron content, expressed as a percentage by mass, is calculated to four decimal places using the equation.

$$\text{Fe (II) percent (m/m)} = \frac{V \times 0.0055847}{M} \times 100$$

Where:

V = is the volume, in milliliters, of potassium dichromate solution (9.2.8) required for the titration

M = mass of the sample taken (g)

**10.6.2** Calculate the Fe (II) content to four decimal places. Carry out independent duplicate analysis. The final results shall be reported to two decimal places, based on the directions given in clause 7.4.

## 10.7 Repeatability (r) and Permissible Tolerance (R)

**10.7.1** The repeatability within a laboratory (r) of the Fe (II) content expressed by the following regression equation based on the arithmetic mean of the two independent duplicate values Fe (II) percent.

$$r = 0.0600 + 0.0153 \times \text{Fe (II) \%}$$

**10.7.2** The permissible tolerance between the laboratories (R) of the Fe(II) content based on the arithmetic mean of the final results reported by the two laboratories. Fe (II) percent is expressed by the following regression equation:

$$R = 0.1806 + 0.0215 \times \text{Fe (II) \%}$$

**10.7.3** The agreement of the final results reported by the two laboratories shall be decided according to 4.3.

## **10.8 Oxide Factor**

$$(\text{Fe II}) \times 1.2865 = \text{FeO\%}$$

$$\text{FeO} \times 3.2227 = \text{Fe}_3\text{O}_4 \%$$

## **11 DETERMINATION OF ALUMINA BY EDTA TITRIMETRIC METHOD**

### **11.1 Outline of the Method**

**11.1.1** From the solution of the ore, iron is removed by sodium hydroxide precipitation. The filtrate containing the alumina is acidified to a specific pH and then it is complexed with excess of EDTA. The excess EDTA is back titrated with standard zinc acetate solution using xylenol orange indicator.

### **11.2 Reagents**

**11.2.1** *Hydrochloric acid* – sp. gr. 1.16 to 1.19 g/ml diluted to 1 : 5 (v/v)

**11.2.2** *Sodium hydroxide solution* - 20 percent.

**11.2.3** *Acetate Buffer* – Dissolve 21.5 g of sodium acetate in about 300 ml water, add 5 ml. of Glacial acetic acid and dilute to 1 litre. Store this solution in a polyethylene bottle.

**11.2.4** *Xylenol Orange Indicator* – Dissolve 0.2 g. xylenol orange in 100 ml. water and add 2 drops of 1:1 hydrochloric acid.

**11.2.5** Bromothymol blue indicator (0.2 percent) – Dissolve 0.2 g of Bromothymol blue indicator in 100 ml. of distilled water.

**11.2.6** *Standard Zinc Acetate Solution* (0.025 Molar) – Dissolve 5.4875 g of zinc acetate in 500 ml of hot water, add few drops of acetic acid to clear up the solution and make up the volume to one litre with distilled water.

**11.2.7** *EDTA Solution* (0.025 Molar) – Dissolve 9.31 g. Disodium salt of EDTA ( $\text{C}_{10}\text{H}_{14}\text{N}_2\text{Na}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$ ) in water and transfer to a 1000 ml volumetric flask, dilute with water to the mark and mix. Store this solution in a polyethylene bottle.

**11.2.8** *Standard  $\text{Al}_2\text{O}_3$*  – Dissolve 0.2646 g. very thin A.R aluminium foil or wire in 10 ml. of concentrated hydrochloric acid and make up to 500 ml (1 ml = 1 mg.  $\text{Al}_2\text{O}_3$ ).

**11.2.9** Dilute Ammonium hydroxide, diluted to 1 : 5 (v/v)-*Ammonium Hydroxide* — rd 0.89

### 11.3 Procedure

- 11.3.1** Pipette out an aliquot equivalent to (0.2 g) of the sample from the main solution in a 250 ml. beaker.
- 11.3.2** Add 20 ml of Sodium Hydroxide (20 Percent) to the above aliquot solution to precipitate Iron as Hydroxide. Add excess of the NaOH solution so that Aluminium Hydroxide which is formed goes into the solution.
- 11.3.3** Heat to boiling with constant stirring and filter (6.2) the solution hot with little filter pulp, into a 500 ml beaker.
- 11.3.4** Wash the residue with hot water 5 to 6 times with a pinch of  $\text{Na}_2\text{CO}_3$ , cool the filtrate.
- 11.3.5** Adjust the pH to 2.5 of the filtrate solution by addition of dilute Hydrochloric Acid.
- 11.3.6** Add by means of a pipette, an excess of 0.025M EDTA (25 ml is sufficient) to the filtrate (2.5 pH). Boil the contents for 10 to 15 minutes and cool. Then adjust the pH 5 to 5.5 by drop wise addition of dilute ammonia. (use Bromothymol blue indicator to get the desired pH, the colour change is from yellow to light green). Use of pH meter also recommended. Add about 15 ml of ammonium fluoride solution and heat the contents to boiling to liberate the complexed EDTA. Boil gently for about 5 min. Cool thoroughly. Add about 1 g of ammonium acetate and titrate the liberated EDTA with zinc solution before adding about 3 drops of xylenol orange indicator solution. Record the titre in ml.

Ammonium Fluoride Solution - Dissolve 10 g of ammonium fluoride in 100 ml of water in a polythene beaker. Prepare fresh every day

- 11.3.7** Add 25 ml of sodium acetate buffer (pH 5.2), and few drops of xylenol orange indicator and titrate against the standard zinc acetate solution. The colour changes from golden yellow to orange. Record the titrate value (A)
- 11.3.8** Carry out the blank titration using 25 ml of EDTA against standard zinc acetate solution. Record the titrate value (B).

### 11.4 $\text{Al}_2\text{O}_3$ Equivalent of Zinc Acetate Solution

Take 5 ml standard aluminium solution (equivalent of 5 mg of  $\text{Al}_2\text{O}_3$ ) in a beaker. Add 25 ml of EDTA solution and make up the volume to nearly 200 ml and boil for 10 minutes and cool. Adjust the pH to 5 - 5.5 (by using Bromothymol indicator). Add 25 ml of sodium acetate buffer and few drops of xylenol orange indicator when yellow colour will develop. Titrate with zinc acetate solution to orange end point.

$$\frac{1 \text{ ml zinc acetate solution}}{1} = \frac{5 \text{ mg of Al}_2\text{O}_3}{(B-A) \times 1000} = X$$

where

A= ml Zinc acetate solution required for titration after adding 25 ml EDTA solution to the 5 ml standard  $\text{Al}_2\text{O}_3$  solution.

B= ml zinc acetate equivalent to 25 ml EDTA solution (blank)

X= $\text{Al}_2\text{O}_3$  Equivalent of Zinc Acetate Solution

### 11.5 Expression of the Result

$$\text{Al}_2\text{O}_3, \text{ percent} = \frac{X \times (B - A) \times 100}{\text{mass of the sample in g}}$$

## 12. DETERMINATION OF PHOSPHORUS BY THE QUINOLINE – PHOSPHOMOLYBDATE METHOD (WILSON METHOD)

### 12.1 Outline of the Method

The sample is decomposed with hydrochloric and nitric acid. The acid is neutralized with sodium hydroxide (NaOH) and the precipitate is re-dissolved in hydrochloric acid in presence of citric acid. The phosphorus is precipitated as yellow coloured quinoline phosphomolybdate. The precipitate is washed and dissolved in excess of standard alkali solution. The unreacted alkali is back titrated against standard hydrochloric acid.

### 12.2 Reagents

**12.2.1** Conc. Hydrochloric acid – RD = 1.16 (conforming to IS 265 : 1976)

**12.2.2** Conc. Nitric acid – RD – 1.42 (conforming to IS 264 : 1976)

**12.2.3** Sodium-hydroxide solution (10 percent)

**12.2.4** Dilute hydrochloric acid (1 : 1)

**12.2.5** Citric acid

**12.2.6** Citromolybdate Solution

Stir 54 gm of A.R.  $\text{MoO}_3$  with 200 ml distilled water, add 11 g of A.R. 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 add 140 ml pure HCl and add the molybdate solution to the acid solution while stirring, cool and filter through a pulp pad, if necessary, and dilute to 1 litre. The solution is blue or green in colour. Add dropwise a dilute 0.5 to 1 percent solution of  $\text{KBrO}_3$  until the blue colour disappears.

**12.2.7** Quinoline Hydrochloride Solution

Take 60 ml conc. HCl and 300-400 ml. water in a one-litre beaker and warm it to 70-80°C. Pour 50 ml. 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, if necessary.

#### **12.2.8 Sodium Hydroxide Solution 0.1 N**

Dissolve 4 g. of sodium hydroxide in 1 litre of freshly boiled and cooled water of (free from CO<sub>2</sub>) and mix well. Protect the solution from CO<sub>2</sub>.

#### **12.2.9 Phenolphthalein Indicator Solution**

Dissolve 0.5 g phenolphthalein in 100 ml of 60 percent alcohol.

#### **12.2.10 Standard sodium carbonate (0.1N).**

Dissolve 5.3 g anhydrous sodium carbonate (99.9 percent min), dried to 260°C till constant mass, in water & dilute to 1 litre.

#### **12.2.11 Standard Hydrochloric Acid (0.1 N)**

Dilute 11 ml. of concentrated hydrochloric acid to 1 litre and standardize against standard sodium carbonate solution.

**12.2.11.1** To standardize standard hydrochloric acid (**12.2.11**), pipette out 25 ml. sodium carbonate (**12.2.10**) in 250 ml conical flask, add 2 to 5 drops of methyl orange indicator (0.1% in water) and titrate against standard hydrochloric acid to the first appearance of orange colour. Calculate the normality of hydrochloric acid.

$$\text{(N) Normality of hydrochloric acid} = \frac{2.5}{V}$$

where

V = Volume in ml. of hydrochloric acid.

### **12.3.1 Procedure**

Dissolve 0.5 g. of sample in 25 ml 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 percent Sodium Hydroxide (NaOH) solution using litmus paper. Re-dissolve the precipitate formed in dilute hydrochloric acid. Add about 5 ml dilute hydrochloric acid in excess. Dilute the solution to 150 ml with DM water. Add about 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 to 2 hours. It is better to keep it overnight.

**12.3.2** Collect the precipitate on a pad of filter paper pulp under suction. Wash the conical flask 4 to 5 times with cold water and transfer this water to filtering

pad. Wash the precipitate 4 to 5 times with cold water (till it is free from acid). Transfer the precipitate along with filter paper pad to the original flask.

**12.3.3** Add 50 ml. DM water. Add known excess of 0.1N Sodium Hydroxide (NaOH) solution to dissolve the yellow precipitate of quinoline phosphomolybdate completely. Add 2 to 3 drops of phenolphthalein indicator. Titrate this against standard hydrochloric acid solution (0.1N) to a colourless end point. (A)

**12.3.4** Carry out blank on the same quantity of sodium hydroxide solution which was added to the test and titrate with standard hydrochloric acid, using 3 to 4 drops of phenolphthalein indicator solution (B) (blank)

## 12.4 Calculation

$$\text{Phosphorus, percentage} = \frac{(B-A) \times 0.001193 \times N \times 100}{(m) \text{ mass of the sample taken}}$$

$$P_2O_5 = P \times 2.2914$$

Calculate the phosphorus percent four places of decimal. Carry out independent analysis. The final result shall be reported to three decimal places based on the directions given in Clause 5.6

## 12.5 Advantages

**12.5.1** The main advantage over the ammonium phospho-molybdate method are :

- (i) Quinoline phospho-molybdate method can be applied for the determination of phosphorous in the sample by suppressing silica.
- (ii) Quinoline phosphomolybdate is less soluble and has a constant composition.

**12.5.2** Precipitate can be washed with plain cold distilled water and no additives are needed to avoid peptization.

## 12.6 Precaution

**12.6.1** Ammonium salts interfere and must be eliminated by means of sodium nitrite or sodium hypobromite.

**12.6.2** Sulphuric acid leads to high and erratic results.

**12.6.3** MoO<sub>3</sub> reagent should be of AR grade and from standard company. It is observed that due to presence of ammonia, some reagents give erratic results. Proportion of reagents given for the preparation of citromolybdate should be strictly adhered to.

## **13 DETERMINATION OF SUPHUR (0.01 percent to 1.00 percent)**

### **13.1 Outline of the Method**

The sample is decomposed with potassium chlorate and hydrochloric-nitric acid mixture, and the solution is evaporated to dryness after adding hydrochloric acid. The soluble salt is dissolved in hydrochloric acid, and the insoluble residue is filtered off. Silica volatilizes from the insoluble residue with hydrofluoric acid, the non-volatile matter is fused with sodium carbonate and the melt is leached with warm water and filtered. The carbonate in the filtrate is acidified and combined with the main solution.

**13.1.1** Zinc or Aluminium metal is added to reduce the bulk of trivalent Iron to Bivalent Iron, and acidity is adjusted.

**13.1.2** Barium Chloride solution is added and the barium sulphate precipitate is filtered off. The precipitate is ignited at 950° C until constant mass is obtained, and the amount of sulphur is calculated from the mass.

### **13.2 Reagents**

NOTE — Distilled or De-ionised water shall be used in the preparation of reagents and throughout the analysis. All reagents shall be of recognized analytical reagent quality.

**13.2.1** *Potassium Chlorate* – Powder

**13.2.2** *Acid Mixture* – Hydrochloric Acid (4) + Nitric Acid (1).

**13.2.3** *Concentrated Hydrochloric Acid* – see **8.2.1**

**13.2.4** *Dilute Hydrochloric Acid*- 10: 5, 1: 1, 2: 100.

**13.2.5** *Ammonium thiocyanate Solution* ( $\text{NH}_4\text{CNS}$ ) – 100 g/l (m/v).

**13.2.6** *Zinc Powder* (99.9 percent pure min.) or *Aluminium foil* (99.9 percent pure min.)

**13.2.8** *Sodium nitrate Solution* – saturated solution in water.

**13.2.9** *Concentrated Nitric acid* – see 9.8.2.2

**13.2.10** *Hydrofluoric Acid* – 40 Percent and RD - 1.13 g/ml.

**13.2.11** *Sodium carbonate* – solid

**13.2.12** *Sodium carbonate solution* (20g  $\text{Na}_2\text{CO}_3$  /l) – Store in a plastic bottle.

**13.2.13** *Methyl Orange solution*- Dissolve 0.1 g of methyl orange in 100 ml of water.

**13.2.14** *Zinc* – Use zinc with the lowest content of sulphur and of 1-3 mm size.

**13.2.15 Barium Chloride Solution (100 g/l)**

Dissolve 100 g of crystalline barium chloride ( $\text{BaCl}_2$ ) in 1 litre of water, cover and allow the solution to cool overnight to room temperature. Store the solution in a plastic bottle and filter through a close texture filter paper the required volume before each use.

**13.2.16 Hydrochloric Acid Wash Solution Containing Barium Chloride**

Filter 10 ml of the barium chloride solution (13.2.15) through a closed texture filter paper, and dilute with 1 litre of dilute hydrochloric acid (2 : 100)

**13.2.17 Silver Nitrate Solution (10 g  $\text{AgNO}_3$ /l) – (m/v)**

**13.3 Procedure**

**13.3.1 Decomposition of Test Portion**

Weigh 5.0 g of the sample. Place the test sample portion in a 500 ml beaker, add 1 g of potassium chlorate and 3 to 4 ml of water, and shake thoroughly. Add 70 ml of acid mixture and heat gently to de-compose the ore. Evaporate the solution on a hot-plate heated to 110 to 120 °C to dryness and cool.

**13.3.2** Add 30 ml of dilute hydrochloric acid (1 : 1) and dissolve soluble salts by warming. Add 25 ml of water and boil for about 5 minutes. Filter the solution through a close texture filter paper and wash the paper with warm dilute hydrochloric acid (2 : 100) until iron ion is no longer detected in the washings by test with ammonium thiocyanate solution. Preserve the filtrate as the main solution in a 500 ml beaker.

**13.3.3 Treatment of Residue**

The procedure to be adopted if any insoluble sulphate is expected.

**13.3.4** Place the residue with the filter paper in a platinum crucible, moisten the filter paper with 1 to 2 drops of sodium nitrate solution, heat the crucible carefully and ignite at 800 to 850°C. Allow the crucible to cool, moisten the ignition residue with a few drops of concentrated nitric acid, add about 5 ml of hydrofluoric acid and heat gently to remove silicon dioxide and nitric acid.

**13.3.5** Allow the crucible to cool, add 3 g of sodium carbonate and fuse the residue at  $1000 \pm 50$  °C for about 15 minutes. Allow the crucible to cool, place the crucible containing the melt in a 300 ml beaker, add about 30 ml of warm water and heat to dissolve the melt. Take out the crucible and rinse with water.

**13.3.6** Collect the residue on a close texture filter paper, wash the filter paper several times with sodium carbonate solution, and discard the residue. Combine the filtrate and washings, add dilute hydrochloric acid (1 : 1) in small portions, while stirring to neutralize the solution using 0.5 ml methyl orange solution as

the indicator. Add 30 ml of concentrated hydrochloric acid in excess and combine with the main solution from 13.3.2.

- 13.3.7** Adjust the volume of the main solution to about 300 ml in a 500 ml beaker and heat to about 60 to 70 °C. Add slowly with constant stirring pure zinc powder or small pieces of aluminium foil, till all trivalent iron is reduced. The solution now will turn out to be greenish to colourless. Filter the solution if required through a close texture filter paper (6.2) in a 500 ml beaker. Wash the residue on the filter paper 5 to 6 times with hot water. Add 5 ml of concentrated hydrochloric acid and mix well.

### **13.4 Precipitation of Barium Sulphate**

- 13.4.1** Cover the beaker containing the combined main solution with a watch glass and heat to evaporate the solution to 25 ml. Allow the solution to cool, add 3 ml of dilute hydrochloric acid (1 : 1) and 50 ml of water and heat the solution to dissolve salts. Add 1.0 g of zinc in the portion, while heating on a water bath at 60 to 70°C, to reduce the remaining trivalent iron to bivalent iron. Filter the solution through a close texture filter paper immediately after complete dissolution of the zinc, and wash with dilute hydrochloric acid (2 : 100) to a total volume of 120 ml. Collect the filtrate and washings in 300 ml tall form beaker. Discard the residue.
- 13.4.2** Boil the solution. Add slowly 5 ml of 10 percent barium chloride solution from a burette. Continue boiling for 5 minutes. and then keep in steam bath for 2 hours or preferably overnight.
- 13.4.3** Collect the precipitate of barium sulphate on a close texture filter paper and wash the beaker once with hydrochloric acid wash solution containing barium chloride. Scrap out the precipitate still adhering to the walls of the beaker using rubber-tipped glass rod, transfer to the filter paper with the aid of hydrochloric acid wash solution containing barium chloride and wash out the beaker several times with the same solution. Wash the precipitate on the filter paper with warm water until chloride ion is no longer detected in the washings by test with silver nitrate solution.

### **13.5 Weighing**

- 13.5.1** Place the precipitate from 13.4.3 with the filter paper in tared platinum crucible. Dry at low temperature, ignite to ash carefully at about 500°C. Add 1-2 drops of sulphuric acid (1 : 1) and ignite at about 800°C for about 20 minutes until constant mass is obtained. Allow the crucible to cool at room temperature in a desiccator and weigh as barium sulphate.

### **13.6 Expression of Results**

- 13.6.1** Calculation of Sulphur Content

The sulphur content, as a percentage of Mass is calculated from the following:

$$\text{Sulphur, percent} \quad = \frac{(m_1 - m_2) \times 0.1374 \times 100}{(m/m) \quad m_3}$$

Where,

$m_1$  = mass in g of the platinum crucible with barium sulphate,

$m_2$  = mass in g of the platinum crucible, and

$m_3$  = mass in g of the test portion.

#### **13.6.2 Blank values**

Carry out a blank test and subtract the blank value from the analytical value.

- 13.6.3** Calculate the sulphur content to four decimal places. The mean of the duplicate results shall be reported to three decimal places based on the direction given in clause 5.6, as per the flow sheet given in Annexure A, based on the repeatability value  $r$ .

### **13.7 Repeatability and Permissible Tolerance**

- 13.7.1** The permissible tolerance within a laboratory of the Sulphur content  $r$ , is expressed by the regression equation based on the arithmetic mean of the duplicate values:

$$r = 0.026 \times (S \%) + 0.004$$

- 13.7.1** The permissible tolerance between the laboratories, based on the arithmetic mean of the final results of the two laboratories  $R$ , is expressed by the regression equation:

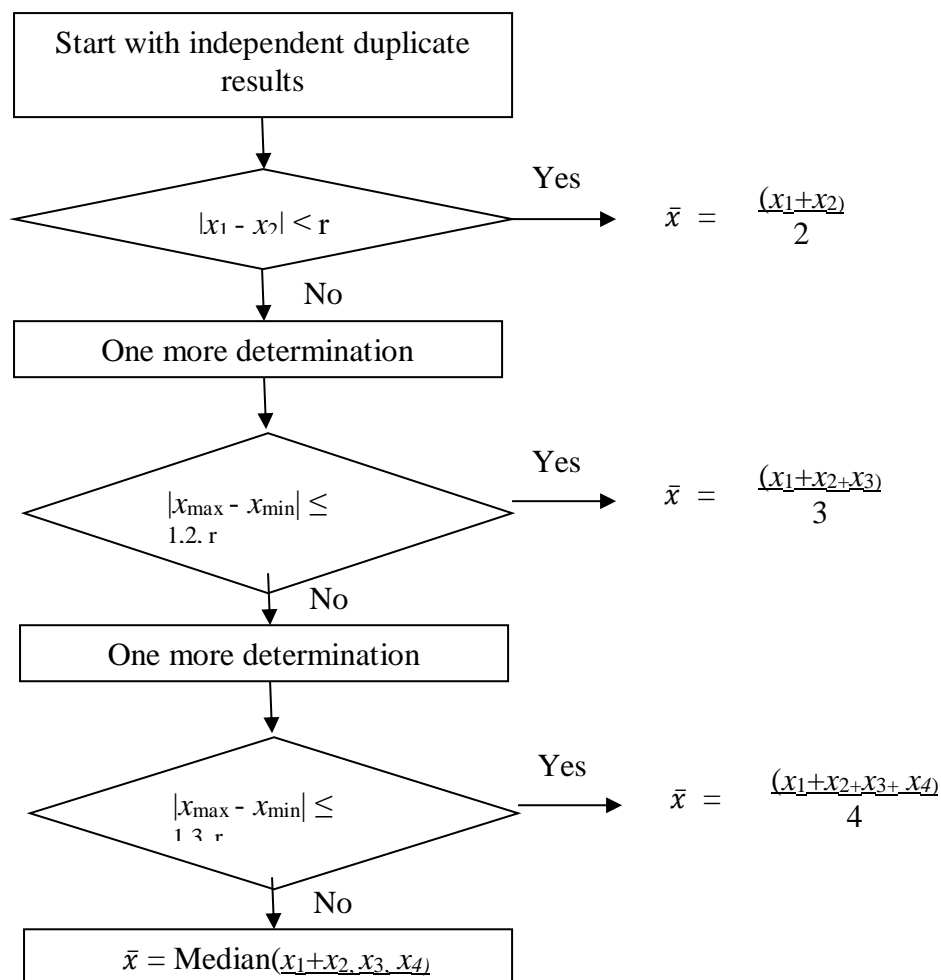
$$R = 0.0270 \times (S \%) + 0.006$$

### **13.8 Oxide Factor**

$$S \% \times 2.50 = SO_3 \%$$

**ANNEXURE-A**  
*(Clause 9.9)*

Flow sheet for the procedure for the acceptance of analytical values for test sample



- 1)  $\bar{x}$  is the mean of independent results
- 2)  $x_1, x_2, x_3, x_4$  are the independent results
- 3)  $r$  is the permissible tolerance with in a laboratory
- 4) If  $x_1 > x_2 > x_3 > x_4$ , median is  $(x_2+x_3)/2$

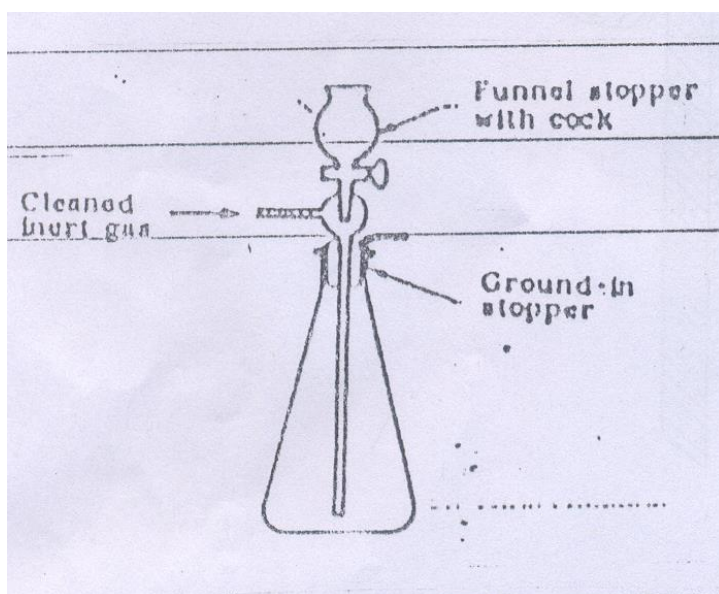


Figure-1  
Decomposition Flask (Gockel safety trap)

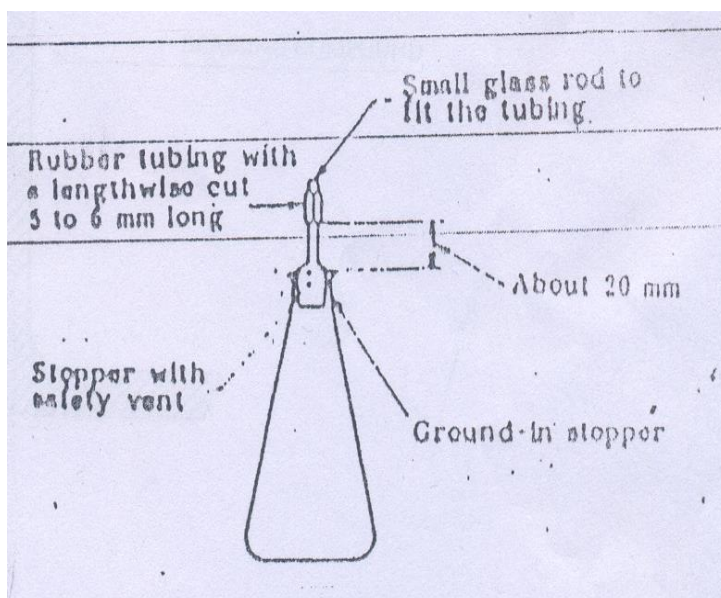


Figure-2  
Simple decomposition Flask (Gockel safety trap)

## ANNEXURE-B

### **Decontamination of mercury from the waste solutions after analysis before discharge to effluent drains.**

To avoid discharging to the environment, the mercury contained in the waste solutions from the determination of iron, such solutions should be collected and processed for the removal of their mercury content.

A suitable treatment system may be constructed as follows:

Three 10 litre plastics bottles are connected as illustrated in Figure 3. (The expansion chamber incorporated in the connecting lines minimizes the risk of pressure increase in the case of a vigorous reaction.) The first two bottles each contain 3 kg of aluminium or iron rods to induce mercury precipitation electrochemically.

The solution discharged from the third bottle is fed to a neutralization vessel before final discarding. Accumulated mercury sludge is removed from time to time and concentrated by decantation before transfer to a recovery plant. The aluminium or iron rods are replaced as necessary.

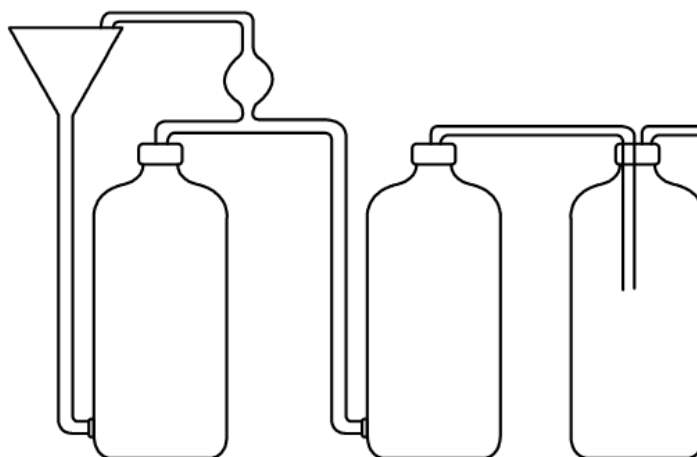


Figure -3 : Apparatus for removal of mercury from waste solutions  
Reference: ANSMANN, W. Arch. Eisenschuttew. 53(10) 1982:390.

ANNEXURE-C  
(clause 9.4.3)

**PREPARATION OF SILVER REDUCTOR**

Take 30 g of silver nitrate in a 600-ml beaker, dissolve in 400 ml of water. Acidify with about 10 ml of concentrated nitric acid (rd-1.42) Immerse in the solution crosswise two rods of Zn each about 15 cm long, 5-6 mm in diameter. Leave the whole thing overnight. Remove the rods and decant off the solution. Wash the silver thoroughly by decantation with dilute sulphuric acid. Then transfer the whole thing to the silver reductor column. The reductor column has the main portion made of pyrex glass tube of 12 cm length and 2 cm diameter. There is a glass stopper at the bottom and the end is drawn to narrow tip. Above the stopper is placed a perforated ceramic disc and some glass wool. (see Figure. 4 ). The upper part of the column is made into a wider beaker like cup of about 6 cm diameter. Transfer the silver to the column ( about 10 cm ), wash with dilute sulphuric acid taking care that no bubbles or air gaps are formed in the column. Drain out the solution and finally wash several times with dilute hydrochloric acid ( 1 N ) before it is used for reduction.

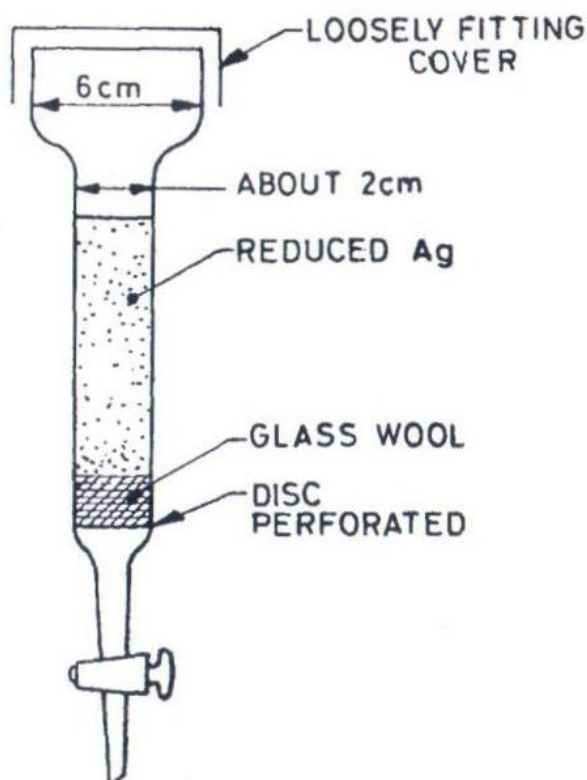


Figure -4 Sketch of Silver Reductor