Draft Indian Standard

METHODS OF CHEMICAL ANALYSIS OF IRON ORES

0. FOREWORD

0.1 This Indian Standard was adopted by the Indian Standards Institution on 14 September 1959, after the draft finalized by the Methods of Chemical Analysis Sectional Committee had been approved by the Structural and Metals Division Council.

0.2 India possesses about one-fourth of the total world reserves of iron ores and is the biggest single country possessing such large quantities of iron ore deposits. She is a major world supplier of the ore and large quantities are regularly exported from the various Indian ports. The exports are expected to mount up with their canalization through the State Trading Corporation of India Ltd. With the setting up of more steel plants in the public sector, India’s consumption of iron ore will increase considerably. The prices paid to the mine owners for the ore are directly linked with the contents of iron, phosphorus, etc. The Sectional Committee, therefore, felt that a standard for the methods of chemical analysis of iron ores will be helpful in co-ordinating the methods followed by the laboratories attached to the various indigenous steel plants and the public analysts engaged in analyzing the export consignments.

0.3 The methods of analysis prescribed in this standard have been prepared with a view that they shall be useful as reference methods. Due consideration has been given, in the preparation of this standard, to the facilities available in the country for such analysis. Furthermore, due weightage had to be given to the need for international co-ordination among standards prevailing in different countries of the world in this field. This consideration led the Sectional Committee to derive assistance from the following standards and publications:

JIS M 8211 TO 8225-1956 METHODS OF CHEMICAL ANALYSIS OF IRON ORE. Japanese Industrial Standards Committee.

1956 BOOK OF ASTM METHODS FOR CHEMICAL ANALYSIS OF METALS. American Society for Testing Materials.

HILLEBRAND, W. F.; LUNDELL, G. E. F.; & BRIGHT, H. A. Inorganic Analysis, 2nd ed. John Wiley & Sons, l953.

FURMAN, N. M. (Ed) Scotts Standard Methods of Chemical Analysis, 5th ed. New York. D. Van Nostrand Co. Inc., 1948.

0.4 This standard requires reference to the following Indian Standards:

IS 264-1950 SPECIFICATION FOR NITRIC ACID

*IS 265-1950 SPECIFICATION FOB HYDROCHLORIC ACID

*IS 266-1950 SPECIFICATIOIN FOR SULPHURIC ACID

*IS 1070-1957 SPECIFICATION FOR DISTILLED WATER

IS 1338-1959 CERTIFIED SAMPLES FOR METALLURGICAL ANALYSIS

*IS 1405-1960 METHODS OF SAMPLING IRON ORE

0.4.1 Wherever a reference to any Indian Standard mentioned under **0.4** appears in this standard, it shall be taken as a reference to the latest version of the standard.

0.5 In reporting the result of a test or analysis made in accordance with this standard, if the final value, observed or calculated, is to be rounded off, it shall be done in accordance with *IS 2-1949 Rules for Rounding Off Numerical Values.

1. SCOPE

1.1 This standard prescribes the methods of determination of moisture, silica, iron, alumina, titanium, manganese, calcium oxide, magnesium oxide, phosphorus, sulphur, ferrous oxide, vanadium and combined water. For export purposes, the determinations of lead, copper, zinc and arsenic are sometimes required. Methods for determination of these elements have also been included.

1.2 Modifications of the procedures for the determination of various constituents have been prescribed, taking into account the variations in the chemical composition as commonly found. However, no account has been taken of the unusual presence of a constituent like chromium which may be rarely found in iron ores.

1.3 The analytical procedures appear in the following order:

	Item No.
Moisture	0
Silica and Preparation of Main Solution	0
Iron	0
a) by the Dichromate (Referee) Method	
b) by the Permanganate (Alternate) Method	
Alumina (Titanium and Vanadium Content is ≤ 0.5 Percent) - by the 'Oxine' (Referee) Method	0
Alumina (Titanium and Vanadium Content is ≤ 0.5 Percent) - by the Thiosulphate-Phosphate (Alternate) Method	0

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*Since revised.

2. SAMPLING

2.1 Samples for the purpose of moisture determination and chemical analysis shall be drawn in accordance with *IS 1405-1960 Methods of Sampling Iron Ore.

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2.2 Preparation of Samples

2.2.1 *Moisture Sample* **-** 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 sides 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.

2.2.2 *Sample for Chemical Analysis* - The laboratory sample, prepared for the purpose of chemical analysis, shall be emptied on a non-absorbent paper like wax paper, mixed thoroughly by rolling and spread uniformly. From this a sufficient quantity of sample shall be taken with a spatula from all sides. It shall be pulverized in an agate mortar, transferred to a glass or aluminium petri dish, dried in an air oven at 105º to 110°C to constant weight and cooled in a desiccator. From this dried sample, different portions shall be weighed out, for analysis, as quickly as possible.

3. QUALITY OF REAGENTS

3.1 Unless specified otherwise, pure chemicals shall be employed in tests, and distilled water (conforming to *IS 1070-1957) shall be used where the use of water as a reagent is intended.

NOTE - 'Pure chemicals' shall mean chemicals that do not contain impurities which affect the results of analysis.

4. GENERAL

4.1 Use of Filter Papers - In the methods prescribed in this standard, relative numbers of Whatman filter paper only have been prescribed, since these are commonly used. However, any other suitable brand of filter papers with the equivalent porosity may be used.

4.2 Method of Reporting - It is the usual practice to report the results of analysis on dried sample (laboratory sample dried at 105º to 110ºC to constant weight). Express the results of moisture, iron, silica, alumina, titanium, vanadium, calcium oxide, magnesium oxide, ferrous oxide and combined water to second decimal place, and the results of phosphorus, sulphur, lead, copper, zinc and arsenic to third decimal place. The results of analysis shall be reported in the following manner. For this purpose conversion factors as indicated shall be used:

Moisture . . . percent

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ANALYSIS OF LABORATORY SAMPLE DRIED AT 105º- 110ºC

Percent

Ferric Oxide	. . .	Fe_2O_3	… Total Iron (Fe) = … percent
Ferrous Oxide	. . .	FeO	
Silica	. . .	SiO_2	
Alumina	. . .	Al_2O_3	
Titanium Dioxide	. . .	TiO_2	… (Ti = … percent)
Vanadium Pentoxi	. . .	V_2O_5	… (V = … percent)
Manganous Oxide	. . .	MnO	… (Mn = … percent)
Calcium Oxide	. . .	CaO	
Magnesium Oxide	. . .	MgO	
Combined Water			
Phosphorus Pentoxide	. . .	P_2O_5	… (P = … percent)
Sulphur Trioxide	. . .	SO_3	… (S = … percent)
Lead	. . .	Pb	
Copper	. . .	Cu	
Zinc	. . .	Zn	
Arsenic	. . .	As	

CONVERSION FACTORS

$Fe_2O_3 = Fe \times 1.4297$

$Fe_2O_3 = FeO \times 1.1113$

$TiO_2 = Ti \times 1.668$

$V_2O_5 = V \times 1.785$

$MnO = Mn \times 1.291$

$P_2O_5 = P \times 2.291$

$SO_3 = S \times 2.497$

4.3 All the determinations should be carried out in duplicate, and blank experiments shall be carried out simultaneously especially for the determination of the trace elements like phosphorus, sulphur, lead, copper, zinc and arsenic, for the purpose of making a corresponding correction in the results of analysis.

4.4 Simultaneously and under the same conditions, a check analysis, especially in the determination of important constituents like iron, phosphorus, etc, shall be made on a certified sample of iron ore prepared in accordance with IS 1338-1959.

5. DETERMINATION OF MOISTURE

5.1 Procedure - Dry a glass or preferably aluminium petri dish in an oven at 105° to 110ºC, cool in a desiccator and weigh. Transfer to this about 100 g of the well-mixed moisture sample (see **2.2.1**). Spread the sample uniformly in the dish and weigh. Dry the sample in an oven at 105° to 110ºC 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.

5.2 Calculation

$$\text{Moisture, percent} = \frac{\text{Loss of weight in g}}{\text{Weight in g of the sample taken}} \times 100$$

6. DETERMINATION OF SILICA AND PREPARATION OF MAIN SOLUTION

6.1 Outline of the Method - The sample is dissolved in concentrated hydrochloric acid and after dehydration of silica by baking, the residue is filtered and ignited. The silica is volatilized by treatment with hydrofluoric acid. In case of ores containing silica above four percent, the residue is fused with sodium carbonate and extracted with hydrochloric acid. The solution is evaporated and silica dehydrated by baking and estimated as usual. For ores containing titanium dioxide above two percent, the hydrochloric acid solution of the sample is fumed with sulphuric acid and filtered. The insoluble residue is fused with potassium bisulphate and extracted with sulphuric acid. The solution is evaporated, silica dehydrated by fuming and then estimated as usual.

6.2 Reagents

6.2.1 *Concentrated Hydrochloric Acid* - sp gr 1.16 (conforming to IS 265-1950).

6.2.2 *Dilute Sulphuric Acid* - 1:1 and 1:20 (by volume).

6.2.3 *Hydrofluoric Acid* - 40 percent.

6.2.4 *Sodium Carbonate* - anhydrous.

6.2.5 *Potassium Bisulphate* - anhydrous.

6.2.6 *Dilute Hydrochloric Acid* - 1:20 (by volume).

6.2.7 *Concentrated Nitric Acid* - sp gr 1.42 (conforming to IS 264-1950).

6.3 Procedure for Ores Containing Titanium Dioxide ≤ 2 percent

6.3.1 Weigh accurately about three grams of the sample and transfer it to a 400-ml tall-form beaker. Add about 35 ml of concentrated hydrochloric acid and a few drops of concentrated nitric acid. Cover with a watch-glass and digest on a hot-plate or a sand-bath. Avoid actual boiling and stir the contents gently and occasionally. Continue digestion until all the ore is attacked and only the silica, with other insoluble matter, remains undissolved. Wash in the watch-glass with a little water.

6.3.2 Add two millilitres of dilute sulphuric acid (1:1), evaporate the contents to dryness and bake the residue at 120ºC for an hour. Cool slightly and take up the residue in 10 ml of concentrated hydrochloric acid. Cover with a watch-glass and warm until the soluble matter has dissolved. Dilute to about 70 to 80 ml with water and boil for a few minutes under cover. Filter the solution through a No. 41 filter paper and transfer all the insoluble matter from the beaker to the filter paper using a rubber-tipped glass rod. Wash the residue three times with hot dilute hydrochloric acid (1:20) and then with hot water till the filtrate is free from chloride. Preserve the filtrate (a).

6.3.3 Treat the residue as follows:

For ores containing silica ≤ 4 percent, proceed as directed in **6.3.3.1**; and

For ores containing silica more than 4 percent, for the highest degree of accuracy and in case of any dispute, proceed as directed in **6.3.3.2.**

6.3.3.1 Dry and ignite the residue in a platinum crucible until all the carbon is burnt off. Cool in a desiccator and weigh. Moisten the residue with a little water and add two to three drops of dilute sulphuric acid (1:1) and 8 to 10 ml of hydrofluoric acid. Evaporate to dryness and ignite for four to five minutes. Cool in a desiccator and weigh. Repeat the procedure adding two to three millilitres of hydrofluoric acid till constant weight is obtained. Treat the residue as directed in **6.5**. The loss in weight (*A*) of the crucible represents silica in the sample. Calculate the silica content from the formula:

$$\text{Silica, percent} = \frac{\text{Loss of weight in g } (A)}{\text{Weight in g of the sample taken}} \times 100$$

6.3.3.2 Dry and ignite the residue in a platinum crucible until all the carbon is burnt off. Fuse the residue with two to three grams of sodium carbonate for 15 to 20 minutes. Extract the fused mass in a 400-ml beaker in about 100 ml of water containing 10 to 15 ml of concentrated hydrochloric acid. Wash the crucible and lid into the same beaker and evaporate the solution to dryness. Bake the residue at 120°C for one hour. Cool slightly and take up the residue in 10 ml of concentrated hydrochloric acid. Cover with a watch-glass and warm until the soluble matter has dissolved. Dilute to 70 to 80 ml with water and boil for a few minutes under cover. Filter through a No. 41 filter paper and transfer all the silica adhering to the beaker by means of a rubber-tipped glass rod. Wash the silica three to four times with hot dilute hydrochloric acid solution and then with hot water until the filtrate is free from chloride. Evaporate the filtrate to dryness and bake the residue at 120°C for an hour. Dissolve the residue in 10 ml of concentrated hydrochloric acid and follow the same procedure of washing the residue as given before. Filter through a No. 41 filter paper, preserve the filtrate (b). Combine the two filter papers containing silica and proceed as directed in **6.3.3.1**.

6.4 Procedure for Ores Containing Titanium Dioxide More Than Two Percent

6.4.1 Weigh accurately about three grams of the sample and dissolve in concentrated hydrochloric acid as given under **6.3.1**. Add to the solution 40 ml of dilute sulphuric acid (1:1). Evaporate the contents on a hot-plate or sand-bath until copious fumes of sulphuric acid are evolved. Cool thoroughly and dissolve the residue in 100 ml of water by boiling until all the soluble matter has dissolved. Filter through a No. 41 filter paper 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 (a).

6.4.2 Dry and ignite the residue in a platinum crucible until all the carbon is burnt off. Cool and fuse the residue with two to three grams of potassium bisulphate for about 15 minutes. Cool and extract the fused mass in a 400-ml beaker containing about 75 ml of 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 of water by boiling until all the soluble matter has dissolved. Filter the solution through a No. 41 filter paper 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 diluted sulphuric acid (1:20). Preserve the filtrate (b). Treat the residue as directed in **6.3.3.1**.

6.5 After the silica has been volatilized by treatment with hydrofluoric acid, fuse the residue, in the platinum crucible, with about one gram of potassium bisulphate for about five minutes. Extract the fused mass in about 60 to 70 ml of hot dilute sulphuric acid (1:20). Wash the crucible and lid into the same beaker. Preserve the solution (c).

6.6 Preparation of Main Solution - Combine the filtrate (a) obtained in **6.3.2** or **6.4.1**, the filtrate (b) obtained in **6.3.3.2** or **6.4.2** and the solution (c) obtained in **6.5**. Concentrate, if necessary, and transfer to a 500-ml volumetric flask, cool and make up to the mark and mix well. This is the solution of about three grams of the sample free from silica which is hereafter referred to as the main solution. From this solution, the determinations of iron, alumina, titanium, manganese, calcium and magnesium are carried out,

7. DETERMINATION OF IRON

7.1 Outline of the Method - Iron is reduced in a boiling solution with stannous chloride solution adding a slight excess of the latter. The excess of stannous chloride is destroyed with mercuric chloride solution, and the reduced iron is titrated either with standard potassium dichromate solution, using sodium diphenylamine sulphonate as an internal indicator or against standard potassium permanganate solution. For accurate work, in case of dispute, and for ores containing vanadium, potassium dichromate method shall be followed.

7.2 Reagents

7.2.1 *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 the solution is complete. Cool, add a few pieces of granulated tin and preserve the solution in an air-tight amber coloured bottle to prevent oxidation.

7.2.2 *Mercuric Chloride Solution* - Prepare a saturated solution of mercuric chloride in water.

7.2.3 *Concentrated Sulphuric Acid* - sp gr 1.84 (conforming to *IS 266-1950).

7.2.4 *Phosphoric Acid* - 85 percent.

7.2.5 *Sulphuric-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.

7.2.6 *Standard Potassium Dichromate Solution* - 0.1 N Dry pure potassium dichromate in an oven at 105° to 110°C for one and a half hours. Cool in a desiccator and transfer exactly 4.9035 g to a one-litre volumetric flask carefully through a funnel using water at room temperature. Wash the funnel thoroughly and dissolve the salt by shaking until the solution is complete. Make up to the mark and mix well. Preserve the solution in an amber-coloured bottle.

7.2.7 *Sodium Diphenylamine Sulphonate Indicator Solution* – Dissolve 0.32 g of barium diphenylamine sulphonate in 100 ml of hot water. Add 0.5 g of sodium sulphate, stir, and filter off the precipitate of barium sulphate. Store in a dark-coloured bottle.

7.2.8 *Zimmermann-Reinhardt Reagent* - Add 140 ml of concentrated sulphuric acid and 140 ml of syrupy phosphoric acid to 720 ml of water. Dissolve 200 g of hydrated manganese sulphate ($MnSO_4$, $4H_2O$) in this solution. While the solution is still hot, add drop by drop potassium permanganate solution (0.1 N) with stirring until the persistent pink colour is obtained.

7.2.9 *Standard Potassium Permanganate Solution* - 0.1 N Dissolve 3.15 g of potassium permanganate in one litre of water. Keep the solution in a glass-stoppered, amber-coloured bottle for 5 to 6 days. Filter through glass wool into a clean glass-stoppered bottle and standardize against sodium oxalate (AR).

7.3 Procedure - By the Dichromate (Referee) Method

7.3.1 Pipette out 50 ml of the main solution obtained in 6.6 into a 500-ml conical flask. Heat to boiling and to the boiling solution, add stannous chloride solution drop by drop with continuous stirring until the solution just becomes colourless. Add two to three drops excess of stannous chloride solution and wash down the sides with a little water. Cool the flask rapidly under running tap water until the contents have cooled down to room temperature.

7.3.2 Add excess of mercuric chloride solution (about five millilitres) and shake the flask. At this stage a silky white precipitate appears. If it fails to appear or if a blackish precipitate appears,

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reject the test. If the precipitate is too much, add further five millilitres of mercuric chloride solution. Keep for about two to five minutes and add 15 ml of sulphuric-phosphoric acid mixture, and dilute to about 250 ml, washing down the sides of the flask. Add three to four drops of sodium diphenylamine sulphonate indicator solution and titrate slowly with standard potassium dichromate solution stirring continuously until the green colour begins to darken. Continue the titration slowly till a drop of the dichromate solution produces a stable violet-blue colouration.

7.3.3 *Calculation*

$$\text{Iron, percent} = \frac{A \times B \times 0.05585 \times 10}{C} \times 100$$

where

A = volume in ml of the standard dichromate solution consumed,
B = normality of the standard dichromate solution, and
C = weight in g of the sample taken.

7.4 Procedure - By the Permanganate (Alternate) Method

7.4.1 Pipette out 50 ml of the main solution (see **6.6**) into a one-litre conical flask and reduce iron as directed in **7.3.1** and finally cool the solution to room tempeature.

7.4.2 Add excess of mercuric chloride solution and stir. At this stage a silky white precipitate appears. If it fails to appear or if a blackish precipitate appears, reject the test. If the precipitate is too much, add further five millilitres of mercuric chloride solution. Keep for about two to five minutes. Now add 30 ml of Zimmermann-Reinhardt reagent and dilute to about 600 ml, washing down the sides of the flask. Titrate immediately with standard potassium permanganate solution with continuous stirring until a drop of the permanganate solution causes a pink colouration which is stable for four to five seconds only.

7.4.3 *Calculation*

$$\text{Iron, percent} = \frac{A \times B \times 0.05585 \times 10}{C} \times 100$$

where

A = volume in ml of the standard permanganate solution consumed,
B = normality of the standard permanganate solution, and
C = weight in g of the sample taken.

8. DETERMINATION OF ALUMINA (TITANIUM AND VANADIUM CONTENT IS ≤ 0.5 PERCENT) BY THE ‘OXINE’ (REFEREE) METHOD

8.1 Outline of the Method - Iron is precipitated as iron sulphide by passing hydrogen sulphide gas through the ammoniacal solution of the sample in presence of tartaric acid which keeps alumina, vanadium and titanium in solution. After filtering iron sulphide and boiling off hydrogen sulphide from the filtrate, alumina is precipitated, from the acetate solution, as 8-hydroxyquinoline complex (oxinate), filtered, dried and weighed. If titanium and vanadium are present in sufficient quantities to affect the weight of aluminium oxinate, the oxinate is ignited strongly and weighed as alumina. This weight is corrected by deducting the weights of titanium dioxide and vanadium pentoxide determined separately.

8.2 Reagents

8.2.1 *Tartaric Acid* - solid.

8.2.2 *Hydrogen Sulphide* - gas.

8.2.3 *Concentrated Ammonium Hydroxide* - sp gr 0.90.

8.2.4 *Ammonium Suiplride Wash Solution* - Add 30 ml of concentrated ammonium hydroxide to one litre of water containing one gram of tartaric acid and pass hydrogen sulphide gas for about 10 minutes. The solution should contain a slight excess of ammonia which may be added, if required.

8.2.5 *Concentrated Hydrochloric Acid* - see **6.2.1**.

8.2.6 *Bromocresol Purple Indicator Solution* - Warm 0.1000 g of bromocresol purple with five millilitres of alcohol (90 percent) until dissolved. Add 100 ml of alcohol (20 percent), 3.7 ml of (exactly 0.05 N) sodium hydroxide solution and dilute with the alcohol to make up to 250 ml.

8.2.7 *Dilute Ammonium Hydroxide* - 1:3 (by volume).

8.2.8 *'Oxine' 8-Hydroxyquinoline Solution* - two percent (*w/v*). Dissolve five grams of 8-hydroxyquinoline in 15 ml of glacial acetic acid by warming and dilute with water to 250 ml.

8.2.9 *Ammonium Acetate* - solid.

8.3 Procedure

8.3.1 Pipette out 100 ml of the main solution as obtained under 6.6 into a 400-ml beaker. Add two grams of tartaric acid and stir until dissolved. Dilute to about 200 ml and pass hydrogen sulphide gas for five minutes. Make the solution strongly ammoniacal with concentrated ammonium hydroxide and continue passing hydrogen sulphide for 15 to 20 minutes, until all iron is precipitated.

8.3.2 Filter the solution through a No. 41 filter paper and wash the precipitate with ammonium sulphide wash solution 6 to 7 times. Reject the precipitate, acidify the solution with concentrated hydrochloric acid and evaporate the filtrate and washings until all hydrogen sulphide is expelled. Filter the precipitated sulphur through a No. 1 filter paper and wash with hot water 6 to 7 times.

8.3.3 Heat and concentrate the filtrate, if necessary, so that the volume is reduced to about 250 ml. Add three to four drops of bromocresol purple indicator solution and add dilute ammonium hydroxide slowly until the colour just turns violet. Allow the solution to cool to about 70°C and add 25 to 30 ml of 'oxine' solution. Now add 7 to 8 g of ammonium acetate slowly, with stirring, and maintain the solution at 70º to 80ºC until the precipitate has coagulated. Filter the precipitate through a dried and weighed Gooch crucible and wash the precipitate with hot water 10 to 12 times. (If aluminium oxinate is to be ignited, it shall be clone in the same Gooch crucible and then weighed.)

8.3.4 If the titanium and vanadium content in the sample is $\leq$ 0.05 percent, dry the precipitate at 130°C in an oven for one to one and a half hours, cool in a desiccator and weigh.

8.3.4.1 *Calculation*

$$\text{Alumina, percent} = \frac{A \times 0.1110}{B} \times 500$$

where

A = weight in g of aluminium oxinate, and
B = weight in g of the sample taken.

8.3.5 If titanium and vanadium content is more than 0.05 percent, dry and ignite the Gooch crucible first slowly and finally very strongly; cool in a desiccator and weigh.

8.3.5.1 *Calculation*

$$\text{Alumina (impure), percent} = \frac{A \times 500}{B}$$

where

A = weight in g of the impure alumina, and
B = weight in g of the sample taken.

8.3.5.2 From the alumina (impure) percent, deduct the percentage of titanium and vanadium calculated as titanium dioxide and vanadium pentoxide respectively. Both of these elements are determined separately (see **11**, **12**, **20** and **21**).

9. DETERMINATION OF ALUMINA (TITANIUM AND VANADIUM CONTENT IS ≤ 0.5 PERCENT) BY THE THIOSULPHATE-PHOSPHATE (ALTERNATE) METHOD

9.1 Outline of the Method - To the solution of the sample, sodium phosphate is added and the acidity adjusted. Sodium thiosulphate, when added in excess, reduces iron to the ferrous state and precipitates alumina as phosphate. Alumina is calculated from the weight of aluminium phosphate.

9.2 Reagents

9.2.1 *Sodium Phosphate* – 10 percent (*w/v*) solution of disodium hydrogen phosphate.

9.2.2 *Concentrated Ammonium Hydroxide* - sp gr 0.90.

9.2.3 *Concentrated Hydrochloric Acid* - see **6.2.1**.

9.2.4 *Sodium Thiosulphate* - solid.

9.2.5 *Glacial Acetic Acid* - 99.5 percent.

9.2.6 *Ammonium Nitrate Solution* - 5 percent *(w/v)*.

9.3 Procedure

9.3.1 Take 100 ml of the main solution as obtained in **6.6**. Add 25 ml of sodium phosphate solution and then add concentrated ammonium hydroxide drop by drop with constant stirring until a slight flocculent precipitate appears, which persists after stirring. Now add concentrated hydrochloric acid, drop by drop with constant stirring until the faint precipitate just disappears. Add about one millilitre of concentrated hydrochloric acid in excess.

9.3.2 Heat the solution, dilute to about 300 ml with hot water and boil. Add about 10 g of sodium thiosulphate, followed by 20 ml of glacial acetic acid. Boil for 30 minutes, filter and wash with ammonium nitrate solution.

9.3.3 Redissolve the precipitate on the filter paper in hot concentrated hydrochloric acid and wash the residue 7 to 8 times with hot water. Reprecipitate aluminium from the solution, filter and wash the precipitate with ammonium nitrate solution as described in **9.3.1** and **9.3.2**.

9.3.4 Transfer the precipitate of aluminium phosphate to a weighed silica or platinum crucible and heat gently until its contents are dry. Ignite the precipitate at a lower temperature (450° to 500°C) at first and then at 950° to 1000°C until constant weight is obtained.

9.4 Calculation

$$\text{Alumina, percent} = \frac{A \times 41.78}{B}$$

where

A = weight in g of aluminium phosphate obtained, and
B = weight in g of the sample represented by the aliquot taken.

10. DETERMINATION OF ALUMINA (TITANIUM AND VANADIUM CONTENT IS MORE THAN 0.5 PERCENT) BY THE ‘OXINE’ METHOD

10.1 Outline of the Method - From the solution of the ore, iron is removed as iron sulphide by passing hydrogen sulphide in ammoniacal solution in presence of tartaric acid which keeps titanium, vanadium and alumina in solution. After boiling off hydrogen sulphide, titanium and vanadium are precipitated with cupferron solution in cold. After filtering the precipitate, the solution is concentrated and cupferron complex destroyed with nitric acid. Alumina is then precipitated from acetate solution as 8-hydroxyquinoline complex (oxinate), filtered, dried and weighed.

10.2 Reagents - In addition to the reagents listed under **8.2**, the following reagents are required.

10.2.1 *Dilute Sulphuric Acid* - 1:1 and 1:20 (by volume).

10.2.2 *Cupferron Solution* - 6 percent. Dissolve 6 g of cupferron [C_6H_5N (NO) ONH_4] in 80 ml of cold water, dilute to 100 ml, and filter through a No. 1 filter paper. Prepare fresh when needed.

10.2.3 *Concentrated Nitric Acid* - *see* **6.2.7**.

10.3 Procedure

10.3.1 Pipette out 100 ml of the main solution of sample obtained in **6.6** into a 400-ml beaker. Add two grams of tartaric acid and remove all iron as sulphide as directed in **8.3.1** and **8.3.2**.

10.3.2 After hydrogen sulphide is boiled off from the filtrate and sulphur filtered, adjust the volume of the solution to about 300 ml. Add 25 ml of dilute sulphuric acid (1:1). Cool to 10º to 15°C and add slowly 25 to 30 ml of freshly prepared cupferron solution with stirring until all titanium and vanadium are precipitated and the excess of reagent is shown by the appearance of a fine precipitate (after complete precipitation of curdy titanium precipitate) which dissolves in excess of the reagent. Let the contents stand for 10 minutes at 10º to 15ºC, filter the precipitate through a No. 41 filter paper, and wash with cold dilute sulphuric acid (1:20), 8 to 10 times. Preserve the precipitate for the determination of titanium (see **12.3.1**).

10.3.3 Evaporate the filtrate to about 50 ml, add slowly and carefully about 10 ml of concentrated nitric acid and continue heating until all cupferron is destroyed. Cool-and dilute the solution to 200 ml with water and complete the estimation of alumina as directed in **8.3.3** and **8.3.4**.

11. DETERMINATION OF TITANIUM (TITANIUM DIOXIDE CONTENT IS ≤ 2 PERCENT) BY THE HYDROGEN PEROXIDE (COLORIMETRIC) METHOD

11.1 Outline of the Method -The method is based on comparison of colour produced by hydrogen peroxide in dilute sulphuric acid solution of the sample with that obtained in a standard solution containing a known amount of titanium. The yellow colour of iron is suppressed by means of phosphoric acid. In case of ores containing vanadium, the mixed oxides (R_2O_3) are precipitated, ignited and fused with sodium carbonate. The fused mass is extracted with hot water and the solution filtered. The precipitate is dissolved in dilute sulphuric acid, and titanium estimated colorimetrically.

11.2 Reagents

11.2.1 *Dilute Sulphuric Acid* - 1:1 and 1:20 (by volume).

11.2.2 *Phosphoric Acid* - 85 percent.

11.2.3 *Hydrogen Peroxide* - 20 volumes.

11.2.4 *Standard Titanium (Stock) Solution* - Ignite pure titanium dioxide for 10 to 15 minutes strongly and cool in a desiccator. Weigh exactly 0.500 g in a platinum crucible and fuse with about 8 to 10 g of anhydrous potassium bisulphate for about 20 minutes. Cool and extract the fused mass in a 400-ml beaker containing about 200 ml of water and 50 ml of dilute sulphuric acid (l:1). Wash the crucible and the lid into the beaker and boil the contents until the solution is complete. Cool and transfer to a 500-ml volumetric flask, make up to the mark with dilute sulphuric acid (1:20) and mix well.

11.2.5 *Standard Titanium (Dilute) Solution (1 ml = 0.05995 mg of Ti)* - Dilute 10 ml of stock solution (*see* **11.2.4**) to 100 ml with dilute sulphuric acid (1:20) in a 100-ml volumetric flask, and mix well.

11.2.6 *Dilute Ammonium Hydroxide* - 1:3 (by volume).

11.2.7 *Sodium Carbonate* - anhydrous.

11.3 Procedure (in Absence of Vanadium)

11.3.1 Pipette out 100 ml of the main solution obtained in **6.6** into a 250 ml beaker. Add 30 ml of dilute suphuric acid (1:1) and evaporate to fumes of sulphuric acid. Cool and dilute to about 70 ml with water. Boil until the solution is complete, cool, transfer to a 100-ml volumetric flask, make up to the mark and mix well. [This solution is also used for colorimetric determination of manganese (*see* 13.3.1).]

11.3.2 Transfer a suitable aliquot (depending on the titanium content) of the solution to a 100-ml Nessler tube (N_1) and add sufficient dilute sulphuric acid (1:20) to make 50 ml. In another 100-ml Nessler tube (N_2), take 50 ml of dilute sulphuric acid (1:20). Add one millilitre of phosphoric acid and two millilitres of hydrogen peroxide solution to both the tubes. Stir the contents and add with a graduated pipette sufficient standard titanium (dilute) solution to the Nessler tube (N_2) until the colours match approximately. Dilute the contents of both the tubes to 100 ml using dilute sulphuric acid (1:20) and mix, compare the intensities of colours in a suitable type of calorimeter.

11.4 Calculation

$$\text{Titanium, percent} = A \times \frac{H_1}{H_2} \times \frac{5}{B} \times \frac{0.5995}{C}$$

where

A = volume in ml of standard titanium (dilute) solution used,
H_1 = height of column of the standard solution,
H_2 = height of column of the solution of the sample,
B = volume in ml of the aliquot taken of the solution prepared in **11.3.1**, and
C = weight in g of the sample taken.

11.5 Procedure (in Presence of Vanadium)

11.5.1 Pipette out 50 ml of main solution obtained in **6.6**, into a 250-ml beaker and dilute to about 150 ml. Heat to boiling and add with stirring dilute ammonium hydroxide solution until all mixed oxides (R_2O_3) are precipitated. Add a slight excess of ammonia and boil for two to three minutes. Filter through a No. 41 filter paper, transferring any precipitate adhering to the sides of beaker with a rubber-tipped glass rod. Wash with hot water 5 to 6 times and discard the filtrate.

11.5.2 Dry and ignite the precipitate in a platinum crucible until all carbon is burnt off. Fuse the residue with about two grams of sodium carbonate for 15 to 20 minutes. Cool and extract the fused mass with about 150 ml of hot water in a 400-ml beaker. Wash in the crucible and lid with a little water. Filter the solution through a No. 40 filter paper and wash the precipitate with hot water 7 to 8 times. Discard the filtrate.

11.5.3 Transfer the precipitate back to the 400-ml beaker. Return the filter paper to the funnel, and dissolve any precipitate in the filter paper with about 50 ml of hot dilute sulphuric acid (1:20), collecting the filtrate in the same beaker. Wash 5 to 6 times with hot water. Add 10 ml of dilute sulphuric acid (1:1) to the beaker and concentrate the solution. Cool and transfer to a 100 ml volumetric flask, make up to the mark and mix well. Complete the estimation as directed under **11.3.2** and **11.4**.

12. DETERMINATION OF TITANIUM (TITANIUM DIOXIDE CONTENT IS MORE THAN TWO PERCENT) BY THE GRAVIMETRIC METHOD

12.1 Outline of the Method - Iron is first separated in ammoniacal solution of the sample with hydrogen sulphide in presence of tartaric acid which keel-s titanium in solution. Titanium is then precipitated in a cold sulphuric acid solution by means of cupferron. The precipitate is filtered, ignited and weighed as titanium dioxide. If vanadium is present, this is separated by fusion with sodium carbonate and extracted with water.

12.2 Reagents

12.2.1 *Tartaric Acid* – solid.

12.2.2 *Hydrogen Sulphide* – gas.

12.2.3 *Concentrated Ammonium Hydroxide* – sp gr 0.90.

12.2.4 *Ammonium Sulphide Wash Solution – see* **8.2.4**.

12.2.5 *Concentrated Hydrochloric Acid – see* **6.2.1**.

12.2.6 *Dilute Sulphuric Acid* – 1:1 & 1:2 (by volume).

12.2.7 *Cupferron Solution – see* **10.2.2**.

12.2.8 *Sodium Carbonate* – anhydrous.

12.2.9 *Sodium Carbonate Wash Solution* – 0.1 percent (*w/v*).

12.3 Procedure

12.3.1 Dry the precipitate preserved under 10.3.2 carefully as it is liable to melt and spray over. Transfer it to a weighed platinum crucible, and ignite carefully first at a low temperature and finally strongly. Cool in a desiccator and weigh as titanium dioxide. If the sample contains vanadium, proceed as given under **12.3.2**.

12.3.2 Fuse the impure titanium dioxide precipitate with two to three grams of sodium carbonate for 15 to 20 minutes. Extract the fused mass with 100 ml of hot water in a 400-ml beaker until the fused mass is completely extracted. Wash the crucible and lid into the beaker and filter the solution through a No. 40 filter paper. Wash the precipitate three to four times with hot sodium carbonate wash solution and then 7 to 8 times with hot ‘water. Dry and ignite the precipitate in a weighed platinum crucible. Cool in a desiccator and weigh as titanium dioxide.

12.4 Calculation

$$\text{Titanium, percent} = \frac{A \times 0.5995}{B} \times 500$$

where

A = weight in g of titanium dioxide, and

B = weight in g of the sample taken.

13. DETERMINATION OF MANGANESE (MANGANESE CONTENT IS ≤ ONE PERCENT) BY THE PERSULPHATE COLORIMETRIC) METHOD

13.1 Outline of the Method - Manganese is oxidized to permanganic acid by the action of potassium persulphate in hot sulphuric acid solution of the sample in presence of silver nitrate and phosphoric acid. The pink colour thus developed is matched with a standard permanganate solution.

13.2 Reagents

13.2.1 *Silver Nitrate Solution* - two percent (*w/v*)

13.2.2 *Potassium Persulphate* - solid.

13.2.3 *Dilute Sulphuric Acid* - 1:1(by volume).

13.2.4 *Phosphoric Acid* - 85 percent.

13.2.5 *Standard Potassium Permanganate Solution* - 0.01 N Prepare potassium permanganate solution (0.1 N) and standardize as given in **7.2.9**. Pipette out 10 ml of this solution into a 100-ml volumetric flask, dilute to the mark with water and mix well.

13.3 Procedure

13.3.1 Pipette out a suitable aliquot (depending on the manganese content) of the sulphuric acid solution, reserved in **11.3.1**, into a 100-ml beaker. Add 5 ml of silver nitrate solution, and heat to boiling. Add two grams of potassium persulphate and stir. As soon as the colour develops, remove from the heat and cool.

13.3.2 Transfer the solution to a loo-ml Nessler tube (N_1). In another 100-ml Nessler tube (N_2), take 40 ml of water and add 10 ml of dilute sulphuric acid. Add one millilitre of syrupy phosphoric acid to both the Nessler tubes. To Nessler tube (N_2) add, with a graduated pipette, standard potassium permanganate solution (0.01 N) until the colours match approximately. Dilute the contents of both the tubes to 100 ml with water and stir. Compare the intensities of colours in a suitable type of colorimeter.

13.4 Calculation

$$\text{Manganese, percent} = A \times B \times 0.01099 \times \frac{500}{C} \times \frac{100}{D} \times \frac{H_1}{H_2}$$

where

A = volume in ml of standard permanganate solution used,

B = normality of standard permanganate solution,

C = volume in ml of the solution of the sample used,

D = weight in g of the sample taken,
H_1 = height of column of the standard solution, and
H_2 = height of column of solution of the sample.

14. DETERMINATION OF MANGANESE (MANGANESE CONTENT IS MORE THAN ONE PERCENT), BY THE BISMUTHATE METHOD

14.1 Outline of the Method - The method consists in oxidizing bivalent manganese to permanganic acid by the use of sodium bismuthate in nitric acid solution. The permanganate formed is titrated with standard ferrous ammonium sulphate solution.

14.2 Reagents

14.2.1 *Dilute Ammonium Hydroxide* - 1:3 (by volume).

14.2.2 *Concentrated Nitric Acid - see* **6.2.7**.

14.2.3 *Sodium Bismuthate* ($NaBiO_3$) - 80 percent, solid.

14.2.4 *Sulphurous Acid Solution* - Make approximately five percent solution of sulphur dioxide in water.

14.2.5 *Dilute Nitric Acid* - 3:97 (by volume).

14.2.6 *Standard Ferrous Ammonium Sulphate Solution* - 0.02 N. Dissolve about 8 g of pure ferrous ammonium sulphate [$Fe(NH_4)_2 (SO_4)_2, 6H_2O$] in water containing five millilitres of dilute sulphuric acid (1:1) and make up to one litre. Mix well and keep in a glass-stoppered, amber-coloured bottle.

14.2.7 *Phosphoric Acid* - 85 percent.

14.2.8 *Standard Potassium Permanganate Solution* - 0.02 N. Pipette out 50 ml of 0.1 N potassium permanganate solution, prepared and standardized as given in **7.2.9** into a 250-ml volumetric flask. Make up to the mark with water and mix well.

14.3 Procedure

14.3.1 Pipette out 50 ml of the sulphuric acid solution reserved in **11.3.1** into a 250-ml beaker and neutralize with dilute ammonium hydroxide solution until a persistent precipitate is formed. Just dissolve the precipitate with concentrated nitric acid and add 30 ml of the acid in excess. Boil the solution and add 0.5 g of sodium bismuthate. Boil for two to three minutes and dissolve the precipitated oxides of manganese in sufficient amount of sulphurous acid until the solution is clear. Boil to expel sulphur dioxide and oxides of nitrogen. Dilute to about 100 ml with water and cool the solution to 10° to 15°C.

14.3.2 Add about one gram of sodium bismuthate, stir and allow to stand for two to three minutes. Dilute with 75 to 100 ml of cold water at 10° to 15°C and filter immediately through a Gooch crucible. Wash with cold dilute nitric acid (3:97) until the washings are colourless. Reject the insoluble residue. The temperature of the filtrate shall be maintained between 10” and 15°C.

To the filtrate, add a measured excess of standard ferrous ammonium sulphate solution and stir. Add two millilitres of syrupy phosphoric acid and immediately titrate with the standard potassium permanganate solution until a stable pink coiouration is obtained.

14.3.3 Carry out a blank determination through all stages of the method, using the same amount of ferrous ammonium sulphate and phosphoric acid and titrate with standard permanganate solution.

14.4 Calculation

$$\text{Manganese, percent} = \frac{(A-B) \times C \times 0.01099 \times 10}{D} \times 100$$

where

A = volume in ml of standard permanganate solution required for the blank test,

B = volume in ml of standard permanganate solution consumed in the test,

C = normality of standard permanganate solution, and

D = weight in g of the sample taken.

15. DETERMIYATION OF CALCIUM OXIDE BY THE OXALATE (VOLUMETRIC) METHOD

15.1 Outline of the Method - From the solution of the sample, iron, aluminium, titanium and vanadium are first separated as hydroxides with ammonia. Manganese, which remains in solution, is also separated as hydroxide with bromine and ammonia. Calcium is then precipitated in ammoniacal solution with ammonium oxalate. The calcium oxalate is filtered, washed and determined volumetrically by titration with standard potassium permanganate solution.

15.2 Reagents

15.2.1 *Bromine Water* - saturated solution.

15.2.2 *Ammonium Chloride* - solid.

15.2.3 *Concentrated Ammonium Hydroxide* - sp gr 0.90.

15.2.4 *Ammonium Hydroxide Wash Solution* - Add five millilitres of concentrated ammonium hydroxide to one litre of water.

15.2.5 *Dilute Hydrochloric Acid* - 1:20 and 1:2 (by volume).

15.2.6 *Bromine* - liquid.

15.2.7 *Ammonium Oxalate Solution* - saturated.

15.2.8 *Dilute Sulphuric Acid* - 1:1 (by volume).

15.2.9 *Standard Potassium Permanganate Solution* - 0.05 N. Standardized against sodium oxalate.

15.3 Procedure

15.3.1 Pipette out 100 ml of the main solution as obtained in. **6.6** into a 400-ml beaker. Add 10 ml of bromine water and five grams of ammonium chloride. Boil the solution until the excess of bromine is expelled. Remove from the heat and neutralize with concentrated ammonium hydroxide until the hydroxides of iron, aluminium, titanium, etc, are completely precipitated and a slight excess of ammonia remains. Keep the solution just below boiling for three to four minutes, filter through a No. 41 filter paper and wash four times wtth hot ammonium hydroxide wash solution. Preserve the filtrate (a).

15.3.2 Transfer the precipitate of hydroxides of iron, aluminium, titanium, etc, back to the beaker in which they were precipitated using a jet of water. Wash the filter paper with hot dilute hydrochloric acid (1:20) until all the precipitate on the filter paper is dissolved, collecting the filtrate in the same beaker in which the bulk of the precipitate was I transferred. Wash the filter paper three to four times with hot water. Heat .the filtrate till all the hydroxides are dissolved, adding more dilute hydrochloric acid, if required. Add two to three grams of ammonium chloride and heat to boiling. Reprecipitate the hydroxides of iron, aluminium, titanium, etc, filter and wash as in **15.3.1**. Preserve the filtrate (b) and discard the precipitate.

15.3.3 Combine the filtrates (a) and (b) preserved in **15.3.1** and **15.3.2** respectively and concentrate to about 200 ml. Make the solution slightly acidic with dilute hydrochloric acid (1:2) and cool to room temperature. Add about 05 ml of liquid bromine. Stir and keep for three to four minutes. Make the solution strongly ammoniacal with concentrated ammonium hydroxide. Boil for 10 minutes and filter the precipitated hydroxide of manganese through a No. 41 filter paper. Wash the precipitate 6 to 7 times with hot water and discard the precipitate.

15.3.4 Concentrate the filtrate and washings to 250 ml and make the solution ammoniacal. Bring to the boil and add 10 to 15 ml of saturated ammonium oxalate solution. Continue boiling for about 10 minutes and then keep in boiling water bath for about two hours, keeping the solution distinctly ammoniacal. Filter off the precipitate of calcium oxalate through-a No. 40 filter paper and wash with water at room temperature four to five times. Transfer the precipitate back to the beaker in which calcium was precipitated. Dissolve in 50 ml of hot dilute hydrochloric acid (1:2) and precipitate calcium as before. Filter and wash with water at room temperature until the filtrate is free from oxalate. Preserve the filtrate and washings, from the first and the second precipitation, for the determination of magnesium (*see* **16.3.1**).

15.3.5 Transfer the precipitate again to the beaker in which calcium was precipitated by puncturing the filter paper, washing down with 15 ml of dilute sulphuric acid and finally 5 to 6 times with a jet of hot water to bring the calcium oxalate into solution. Dilute the contents of the beaker to about 200 ml, and heat to 75° to 80°C. Titrate with standard potassium permanganate solution until a stable pink colour is obtained.

15.4 Calculation

$$\text{Calcium oxide, percent} = \frac{A \times B \times 0.02803}{C} \times 500$$

where

A = volume in ml of standard permanganate solution consumed,

B = normality of standard permanganate solution, and

C = weight in g of the sample taken.

16. DETERMINATION OF MAGNESIUM OXIDE BY THE PYROPHOSPHATE (GRAVIMETRIC) METHOD

16.1 Outline of the Method - After the calcium is removed from solution of the ore by double precipitation, magnesium is precipitated from the combined filtrate by microcosmic salt in ammoniacal solution. The precipitate is filtered, washed, ignited and weighed as magnesium pyrophosphate.

16.2 Reagents

16.2.1 *Concentrated Hydrochloric Acid - see* **6.2.1**.

16.2.2 *Methyl Orange Indicator Solution* - Dissolve 0.05 g of methyl orange in 100 ml of alcohol.

16.2.3 *Microcosmic Salt Solution* ($NaNH_4HPO_4$) - 10 percent (*w/v*), freshly prepared.

16.2.4 *Concentrated Ammonium Hydroxide* - sp gr 0.90.

16.2.5 *Dilute Ammonium Hydroxide* - 1:20 (by volume).

16.3 Procedure

16.3.1 Evaporate the acidified filtrate preserved in **15.3.4** to about 200 ml. Add two to three drops of methyl orange indicator solution and about two millilitres of concentrated hydrochloric acid till acidic. Add 20 ml of freshly prepared microcosmic salt solution and cool to room temperature. Add concentrated ammonium hydroxide with constant stirring until the colour changes to yellow, then add 10 to 15 ml of concentrated ammonium hydroxide for every 100 ml of the solution and continue stirring until magnesium is precipitated. Let the solution stand for 6 hours or preferably overnight.

16.3.2 Filter the precipitate through a No. 40 filter paper and wash with dilute ammonium hydroxide solution until the filtrate is free from chloride. Dry and ignite the precipitate in a weighed silica crucible carefully at about 450°C until carbon is burnt off and finally at about 900°C for about half an hour. Cool in a desiccator and weigh.

16.4 Calculation

$$\text{Magnesium oxide, percent} = \frac{A \times 0.3621}{B} \times 500$$

where

A = weight in g of magnesium pyrophosphate, and

B = weight in g of the sample taken.

17 DETERMINATION OF PHOSPHORUS BY THE MOLYBDATE (ALKALIMETRIC) METHOD

17.1 Outline of the Method - The sample is dissolved in hydrochloric acid and evaporated to dryness. The dry mass is taken up in concentrated nitric acid and the insoluble matter filtered off. Any phosphorus lost in the insoluble matter is recovered. The phosphorus is then precipitated as ammonium phosphomolybdate. The precipitate is filtered, washed, and dissolved in excess of standard alkali solution. The unreacted alkali is back titrated against standard acid.

17.2. Reagents

17.2.1 *Concentrated Hydrochloric Acid* - *see* 6.2.1.

17.2.2 *Ammonium Bromide* - solid.

17.2.3 *Concentrated Nitric Acid* - *see* 6.2.7.

17.2.4 *Dilute Nitric Acid* - 1:100 (by volume).

17.2.5 *Dilute Sulphuric Acid* - 1:1 (by volume).

17.2.6 *Hydrofluoric Acid* - 40 percent.

17.2.7 *Sodium Carbonate* - anhydrous.

17.2.8 *Concentrated Ammonium Hydroxide* - sp gr 0.90.

17.2.9 *Hydroxylamine Hydrochloride Solution* - 15 percent (*w/v*).

17.2.10 *Ammonium Molybdate Solution* - Add solution (A) (*see* **17.2.10.1**) slowly and with constant stirring to solution (B) (*see* **17.2.10.2**) kept cool in a cold water-bath. Add 10 ml of ammonium phosphate (one gram per litre) and keep the solution at least for 24 hours. Filter the solution through a No. 1 filter paper before use.

17.2.10.1 *Solution (A)* - Dissolve 100 g of molybdic acid (MoO_3, 85 percent) or 118 g of ammonium molybdate in a mixture of 145 ml of concentrated ammonium hydroxide and 270 ml of water. Cool the solution.

17.2.10.2 *Solution (B)* - Add 490 ml of concentrated nitric acid to 1150 ml of water and cool.

17.2.11 *Potassium Nitrate Wash Solution* - one percent (*w/v*).

17.2.12 *Sodium Hydroxide Solution* – 0.1 N approximately.

17.2.13 *Phenolphthalein Indicator Solution* - Dissolve 0.5 g of the phenolphthalein in 100 ml of 60 percent of alcohol.

17.2.14 *Standard Hydrochloric Acid* - 0.1 N. Dilute about 11 ml of concentrated hydrochloric acid to one litre and standardize against sodium carbonate.

17.3 Procedure

17.3.1 Transfer 2.5 to 5.0 g (depending on the phosphorus content) of the sample, accurately weighed, into a 400-ml beaker. Digest with 35 to 40 ml of concentrated hydrochloric acid on a hot-plate or sand-bath until the ore is attacked completely. Evaporate the solution just to dryness. If the sample contains arsenic, add five millilitres of concentrated hydrochloric acid and 0.5 to 1.0 of ammonium bromide and evaporate to dryness. Repeat the procedure to expel all arsenic. Add 20 ml of concentrated nitric acid and digest under cover till most of the nitrous fumes are expelled. Remove the cover and evaporate to syrupy consistency. Add 15 ml of concentrated nitric acid and again evaporate to syrupy consistency. Take up the contents in 10 ml of concentrated nitric acid and digest until the soluble matter has dissolved. Dilute to about 100 ml with water and filter through a No. 41 filter paper. Wash the residue 5 to 6 times with hot dilute nitric acid solution. Preserve the filtrate.

17.3.2 Dry and ignite the residue in a platinum crucible until all the carbon is burnt off. Cool and moisten the residue with a few drops of water. Add two to three drops of dilute sulphuric acid and 7 to 8 ml of hydrofluoric acid. Evaporate to dryness. Cool and fuse the residue with one to two grams of sodium carbonate for 10 to 15 minutes. Cool and extract with 70 to 80 ml of hot water containing 8 to 10 ml concentrated nitric acid. Wash in the crucible and lid. If any insoluble residue remains, filter through a No. 40 filter paper and wash with hot water 5 to 6 times. Combine this solution with the filtrate preserved in **17.3.1** and concentrate to 150 ml.

17.3.3 Cool and neutralize with concentrated ammonium hydroxide until a slight persistent precipitate is formed. Redissolve the precipitate in a few drops of concentrated nitric acid, add one to two millilitres in excess, and heat to 70° to 80°C. If the sample contains vanadium, add two millilitres of hydroxylamine hydrochloride solution. Add with stirring 30 to 40 ml of ammonium molybdate solution; 70 ml for every 0.l g of phosphorus pentoxide. Continue stirring till the phosphorus is precipitated. Keep at 50º to 60°C for one hour.

17.3.4 Filter the precipitate through a thick pad of filter paper pulp prepared on a perforated disc in a funnel. Wash the beaker and the precipitate two to three times with dilute nitric acid solution and then with potassium nitrate wash solution till 10 ml of the filtrate collected in a test-tube does not consume more than one drop of 0.1 N sodium hydroxide solution, using a drop of phenolphthalein indicator solution (begin testing the filtrate from third wash). Transfer the pad of paper pulp with the precipitate back to the beaker in which phosphorus was precipitated and wash down any precipitate adhering to the funnel with a jet of water, into the same beaker. Add 50 to 60 ml of water and add with stirring standard sodium hydroxide solution from a burette until all the yellow precipitate has dissolved and the solution is colourless. Add about five millilitres of sodium hydroxide solution in excess and stir. Add three to four drops of phenolphthalein indicator solution and titrate with standard hydrochloric acid until the pink colour is completely discharged.

17.3.5 Carry out a blank on the same quantity of sodium hydroxide solution which was added in the test, and titrating with standard hydrochloric acid, using three to four drops of phenolphthalein indicator solution.

17.4 Calculation

$$\text{Phosphorus, percent} = \frac{(A - B) \times C \times 0.00135}{D} \times 100$$

where

A = volume in ml of standard hydrochloric acid required for the blank test,

B = volume in ml of standard hydrochloric acid required for the sample,

C = normality of standard hydrochloric acid, and

D = weight in g of the sample taken.

18. DETERMINATION OF SULPHUR BY THE GRAVIMETRIC METHOD

18.1 Outline of the Method - The .sample is dissolved in hydrochloric acid after oxidizing all the sulphur with bromine. The insoluble residue is filtered off. If the sample contains barium, the residue is ignited and silica volatilized with hydrofluoric acid. The remaining residue is fused with sodium carbonate and extracted with water. This is added to the original filtrate and sulphur precipitated as barium sulphate.

18.2 Reagents

18.2.1 *Concentrated Hydrochloric Acid – see* **6.2.1**.

18.2.2 *Potassium Bromide* – solid.

18.2.3 *Bromine* – liquid.

18.2.4 *Hydrofluoric Acid* – 40 percent.

18.2.5 *Sodium Carbonate* – anhydrous.

18.2.6 *Concentrated Ammonium Hydroxide* – sp gr 0.90.

18.2.7 *Zinc* – granulated

18.2.8 *Barium Chloride Solution* – 10 percent (*w/v*).

18.2.9 *Dilute Hydrochloric Acid* – 1:100 (by volume).

18.3 Procedure

18.3.1 Weigh accurately about five grams of the sample into a 400-ml beaker. Add one gram of potassium bromide and add three to four millilitres of water to dissolve the bromide. Add about 0.5 ml of liquid bromine and stir gently. Set the solution aside for about 15 minutes with occasional stirring. Now add 35 to 40 ml of concentrated hydrochloric acid and cover the beaker with a watch-glass. Digest on a hot-plate until all the ore is attacked. Wash in the watch-glass with a little water and evaporate to dryness. Bake the residue for about an hour and cool.

18.3.2 Take up the residue in 10 ml of concentrated hydrochloric acid by warming. Dilute to about 100 ml, boil, filter through a No. 41 filter paper and wash with hot dilute hydrochloric acid solution five to six times. Preserve the filtrate. If the insoluble residue contains barium, proceed as given under **18.3.3**.

18.3.3 Dry and ignite the residue in a platinum crucible until all the carbon is burnt off. Cool and moisten the residue with a few drops of water. Add 6 to 7 ml of hydrofluoric acid. Evaporate to dryness and ignite at about 400ºC. Cool and fuse the residue with two grams of sodium carbonate for about 15 minutes. Cool the fused mass and extract with about 80 ml of water. Filter through a No. 41 filter paper and wash with hot water five to six times. Discard the insoluble residue and acidify the filtrate with concentrated hydrochloric acid. Wash the crucible and lid into the beaker. Combine this solution with the filtrate preserved in **18.3.2** and concentrate to about 200 ml. Neutralize the solution with concentrated ammonium hydroxide until a faint persistent precipitate is formed. Redissolve the precipitate in the minimum amount of concentrated hydrochloric acid and add 7 to 8 ml in excess.

18.3.4 Add 5 to 6 g of granulated zinc to the combined solution obtained in **18.3.3** and warm on steam-bath until all iron is reduced to the ferrous state and evolution of hydrogen ceases. Filter through a No. 42 filter paper and wash with hot dilute hydrochloric acid solution three to four times. Concentrate the solution and adjust the acidity so that it contains two percent by volume of hydrochloric acid. Warm it to 50º to 70°C and add 10 ml of barium chloride solution drop wise with constant stirring. Let the solution stand for two hours on the steam-bath and overnight at the room temperature. Filter through a No. 42 filter paper and wash the precipitate with cold dilute hydrochloric acid and then with hot water until free from chloride. Dry and ignite the precipitate in a weighed platinum or silica crucible, cool in a desiccator and weigh as barium sulphate.

18.4 Calculation

$$\text{Sulphur, percent} = \frac{A \times 0.1374}{B} \times 100$$

where

A = weight in g of barium sulphate obtained from the solution of the sample, and

B = weight in g of the sample taken.

19. DETERMINATION OF FERROUS OXIDE BY THE PERMANGANATE METHOD (NOT APPLICABLE TO HIGH TITANIUM OR VANADIFERROUS ORES)

19.1 Outline of the Method - The ore is attacked, in a covered platinum crucible, with sulphuric acid and hydrofluoric acid in an atmosphere of carbon dioxide. The solution thus obtained is diluted and is immediately titrated with standard potassium permanganate solution in presence of dilute sulphuric acid and boric acid.

19.2 Apparatus – The apparatus is illustrated in Fig. 1.

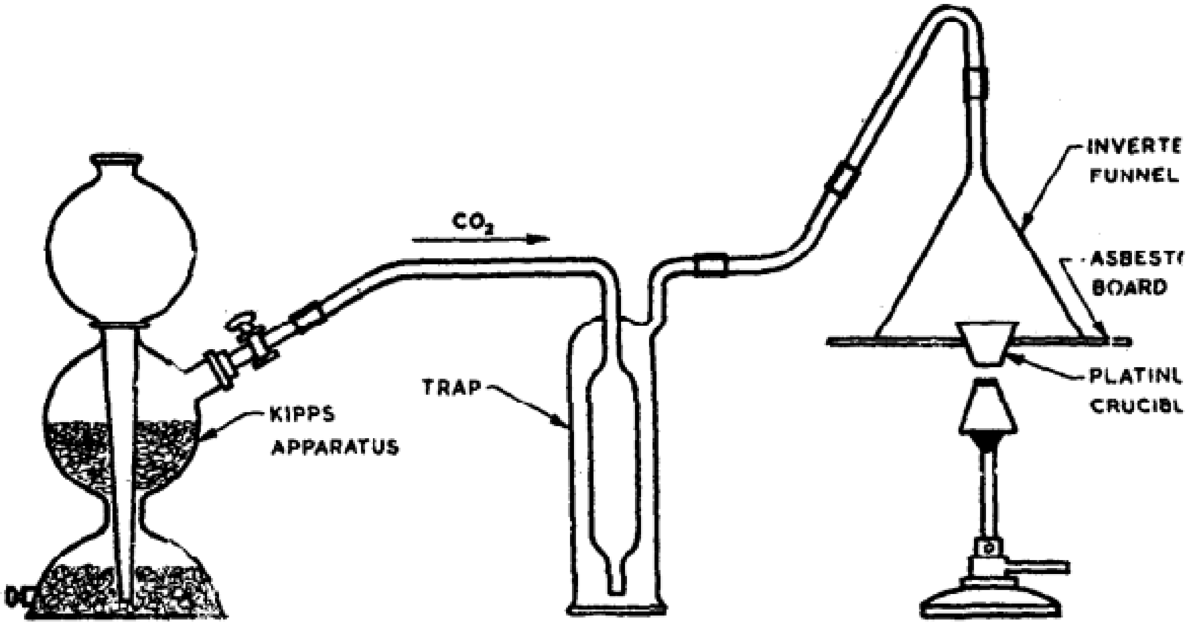

FIG. 1 APPARATUS FOR DETERMINATION OF FERROUS OXIDE

19.3 Reagents

19.3.1 Dilute Sulphuric Acid – 1:1 (by volume).

19.3.2 Carbon Dioxide – gas.

19.3.3 Hydrofluoric Acid – 40 percent.

19.3.4 Boric Acid Solution – Prepare a saturated solution of boric acid in water.

19.3.5 Standard Potassium Permanganate Solution – 0.1 N. *See* **7.2.9**.

19.4 Procedure

19.4.1 Weigh accurately about 0.5 g of the sample and transfer to a platinum crucible. Moisten the sample with freshly boiled and cooled water. Add 15 ml of dilute sulphuric acid and cover the crucible with a close-fitting platinum lid. Fit the crucible tightly into the hole in the centre of the asbestos board (see Fig. 1) so that it passes about half-way through, and the joint between the crucible and the hole is nearly air-tight. Displace the air in the crucible. For this purpose, connect the stem of the tunnel, coated inside with paraffin wax, with the carbon dioxide gas generator and place the funnel over the crucible so that it fits close to the asbestos board, excluding air. Heat the crucible so that the contents boil gently in the atmosphere of carbon dioxide for about 5 minutes. Stop heating, allow the crucible to cool slightly and remove the funnel and the crucible lid. Add about 5 ml of hydrofluoric acid, replace the lid and the funnel quickly, and continue heating so that the contents boil gently for about 10 minutes without interruption. Lift the crucible, without removing the lid and after cooling slightly, plunge it in a 400-ml beaker containing about 200 ml of freshly boiled and cooled water, 10 ml of dilute sulphuric acid and 20 ml of boric acid. Stir thoroughly and titrate immediately with standard permanganate solution until a persistent pink colour is obtained.

19.5 Calculation

$$\text{Ferrous oxide, percent} = \frac{A \times B \times 0.07185}{C} \times 100$$

where

A = volume in ml of standard permanganate solution consumed,

B = normality of standard permanganate solution, and

C = weight in g of the sample taken,

20. DETERMINATION OF VANADIUM (VANADIUM CONTENT IS MORE THAN 0.5 PERCENT) BY THE PERSULPHATE-FERROUS SULPHATE METHOD

20.1 Outline of the Method - The sample is dissolved in concentrated hydrochloric acid and fumed with dilute sulphuric acid. The insoluble residue is filtered off and any vanadium lost in the insoluble residue is recovered. From this sulphuric acid solution of the sample, vanadium, ferrous iron, etc, are oxidized with potassium permanganate solution. An excess of ferrous ammonium sulphate is added which reduces vanadium. The unreacted ferrous ammonium sulphate is oxidized with potassium persulphate and the reduced vanadium titrated with standard potassium permanganate solution.

20.2 Reagents

20.2.1 *Concentrated Hydrochloric Acid* - *see* **6.2.1**.

20.2.2 *Dilute Sulphuric Acid* - 1:1 (by volume).

20.2.3 *Hydrofluoric Acid* - 40 percent.

20.2.4 *Potassium Bisulphate* - solid.

20.2.5 *Potassium Permanganate Solution* - one percent (*w/v*).

20.2.6 *Ferrous Ammonium Sulphate Solution* - 0.1 N. Dissolve about 40 g of ferrous ammonium sulphate [$Fe(NH_4)_2(SO_4)_2, 6H_2O$] in water containing 10 ml of dilute sulphuric acid (1:1) and make up to one litre with water. Mix well and keep in a glass-stoppered, amber-coloured bottle.

20.2.7 *Potassium Persulphate* - solid.

20.2.8 *Potassium Ferricyanide Indicator Solution* - Dissolve about 0.1 g of potassium ferricyanide in 100 ml of water. Prepare fresh as required.

20.2.9 *Standard Potassium Permanganate Solution* - 0.02 N. Pipette out 50 ml of 0.1 N potassium permanganate solution, prepared and standardized as given in **7.2.9**, into a 250-ml volumetric flask, dilute to the mark with water and mix well.

20.2.10 *Phosphoric Acid* - 85percent.

20.3 Procedure

20.3.1 Weigh accurately about two grams of the sample and digest it in a 400-ml beaker with 25 ml concentrated hydrochloric acid. Add 25 ml of dilute sulphuric acid and evaporate until strong fumes of sulphuric acid are evolved. Cool and dilute to about 100 ml with water. Boil until ferric sulphate has dissolved. Filter off the insoluble residue through a No. 41 filter paper and wash with hot water five to six times. Preserve the filtrate.

20.3.2 Dry and ignite the residue in a platinum crucible until all the carbon is burnt off. Cool and moisten the residue with a few drops of water. Add two to three drops of dilute sulphuric acid, and 6 to 7 ml of hydrofluoric acid, and evaporate to dryness. Ignite the residue, cool, and fuse with two to three grams of potassium bisulphate for 15 minutes. Extract the cold melt with 100 ml of water containing 15 ml of dilute sulphuric acid. Wash the crucible and lid into the beaker. Combine this solution with the filtrate preserved in **20.3.1** and concentrate the combined solution to about 200 ml.

20.3.3 Bring the concentrated solution obtained in **20.3.2** to boil and add 10 ml of syrupy phosphoric acid. Add with stirring potassium permanganate solution (one percent) until the pink colour persists. Cool the solution to room temperature. Add an excess of ferrous ammonium sulphate solution until all the vanadium is reduced (as shown by a drop of the solution giving a strong blue colour with a drop of potassium ferricyanide indicator solution). Now add one gram of potassium persulphate and stir for one minute. Titrate with standard permanganate solution to a definite pink colour which does not fade on continued stirring for one minute. Preserve the titrated solution.

20.3.4 For the determination of blank, add to the titrated solution (*see* **20.3.3**) a very dilute ferrous ammonium sulphate solution (0.1 N diluted 5 times) drop by drop until the pink colour is just discharged. Titrate with standard permanganate solution to the same tint as obtained before.

20.4 Calculation

$$\text{Vanadium, percent} = \frac{(A- B) \times C \times 0.05095}{D} \times 100$$

where

A = volume in ml of standard permanganate solution consumed in the test,

B = volume in ml of standard permanganate solution required in the blank,

C = normality of standard permanganate solution, and

D = weight in g of the sample taken.

21. DETERMINATION OF VANADIUM (VANADIUM CONTENT IS ≤ 0.5 PERCENT) BY THE HYDROGEN PEROXIDE (COLORIMETRIC) METHOD

21.1 Outline of the Method - Vanadium is determined by comparing the colours developed by means of hydrogen peroxide with sulphuric acid solution of the sample and with known quantity of vanadium. The yellow colour of iron is suppressed with phosphoric acid and the yellow colou~ developed by titanium is removed with potassium fluoride.

21.2 Reagents

21.2.1 *Dilute Sulphuric Acid* - 1:1 and 1:10 (by volume).

21.2.2 *Hydrogen Peroxide* - 20 volumes.

21.2.3 *Phosphoric Acid* - 85 percent.

21.2.4 *Potassium Fluoride* - solid.

21.2.5 *Standard Vanadium Solution* (1 ml = 0.2 mg of V) - Dissolve 0.4590 g of, accurately weighed, ammonium vanadate in water containing 15 ml of dilute sulphuric acid (1:1) in a one-litre volumetric flask, make up to the mark with water and mix well.

21.3 Procedure

21.3.1 Weigh accurately about one gram of the sample into a 400-ml beaker. Prepare a sulphuric acid solution of the sample as directed in **20.3.1** and **20.3.2** and make up the solution to 250 ml in a volumetric flask and call it solution (*A*). Alternatively, if sufficient quantity of the main solution of the sample obtained in **6.6** is available, pipette out 50 ml of this solution into a 250-ml beaker. Add 20 ml of dilute sulphuric acid (1:1) and evaporate until fumes of sulphuric acid are evolved. Cool and dilute to 50 ml with water. Boil until the solution is complete and call it solution (*B*).

21.3.2 Transfer 50 ml of the solution (*A*) or the entire quantity of solution (*B*) to a 100-ml Nessler tube (N_1). In another 100-ml Nessler tube (N_2), take 50 ml of dilute sulphuric acid (1:10). Add one millilitre of syrupy phosphoric acid, 0.5 g of potassium fluoride and 0.2 ml of hydrogen peroxide to both the tubes. (Undue excess of hydrogen peroxide has a bleaching action on the colour developed by vanadium.) Now add to the Nessler tube (N_2), a sufficient measured quantity of standard vanadium solution until the reddish brown colours match approximately. Make up both the solutions to 100 ml with dilute sulphuric acid (1:10), mix well, and compare the intensities of colours in a suitable type of colorimeter.

21.4 Calculation

$$\text{Vanadium, percent} = C \times \frac{H_1}{H_2} \times 0.0002 \times \frac{100}{D}$$

where

C = volume in ml of standard vanadium solution required,

H_1 = height of column of standard solution,

H_2 = height of column of the solution of the sample, and

D = weight in g of the sample represented by the aliquot of the solution taken.

22. DETERMINATION OF COMBINED WATER

22.1 Outline of the Method - The sample is heated in a tube furnace in a current of dry air. The liberated combined water, which is absorbed in U-tubes containing calcium chloride (anhydrous), is calculated from the increase in the weight of the U-tubes.

22.2 Apparatus - The apparatus as shown assembled in Fig. 2 consists of the following units:

a) *Air Drying Unit* - It consists of a tower (*A*) packed with potash sticks, a gas wash-bottle (*B*) containing concentrated sulphuric acid and a tower (*C*) containing calcium chloride (anhydrous). The main function of the unit is to deliver dry air to the combustion tube (*D*).

b) *Combustion Tube (D)* - It is a silica tube of approximately 500 mm length and 20 to 25 mm inner diameter One end of the combustion tube (*D*) is connected with the air drying unit and the other end to the combined water absorption unit.

c) *Combustion Furnace (E)* - The combustion furnace is an electric furnace having two heating sections and capable of maintaining the first part of the tube between 800º and 900ºC, by means of (E_1). The other section (E_2) heats the end of the combustion tube, containing lead oxides and pumice, at about 250°C.

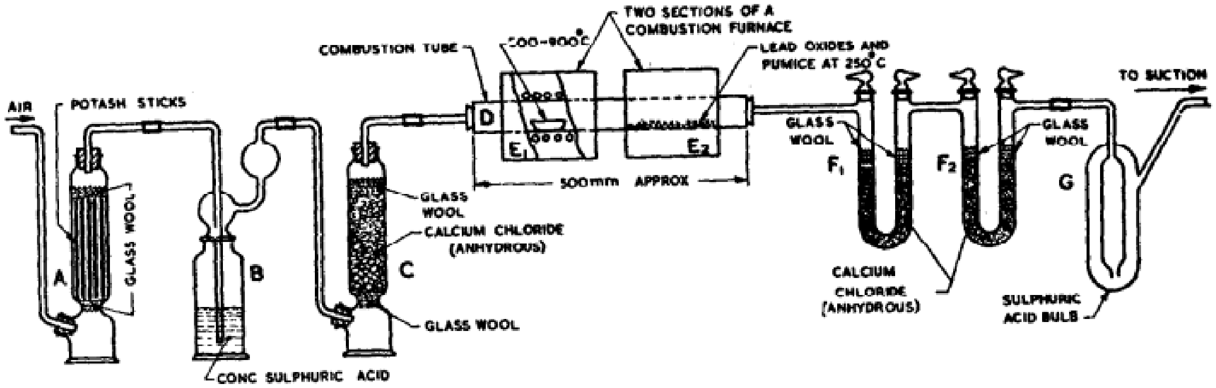

FIG. 2 APPARATUS FOR DETERMINATION OF COMBINED WATER

d) Combined Wafer Absorption Unit - It consists of 2 U-tubes (F_1) and (F_2) packed with calcium chloride (anhydrous) and connected in series on one side with the combustion tube (*D*) and on the other side with a sulphuric acid bulb (*G*). Air is drawn through the apparatus by connecting the end of the bulb (*G*) to suction.

22.3 Reagents

22.3.1 *Potash* - sticks.

22.3.2 *Concentrated Sulphuric Acid - see* **7.2.3.**

22.3.3 *Calcium Chloride Granular* - anhydrous.

22.3.4 *Lead Oxide*

22.3.5 *Lead Peroxide*

22.4 Procedure

22.4.1 Check the assembled apparatus for hermetic sealing. Before beginning the test, disconnect the absorption apparatus and allow the air to flow through the U-tubes at a rate of two to three bubbles per second. Simultaneously, switch on the tube furnace and heat the first section (E_1) to 800° to 900°C. Bring the temperature of the section (E_2) of the furnace, heating a part of the tube containing the lead oxides and pumice, to 250°C. Connect the U-tubes after 30 minutes with the apparatus and pass air for half an hour. Then disconnect the tubes and weigh, after equalizing the pressure by opening the stop-cocks of the tubes for a moment.

22.4.2 Reconnect the U-tubes and pass the air through the apparatus for 30 minutes maintaining the specified temperatures, after which reweigh the tubes. Repeat the procedure, if necessary, until the weights of the tubes (F_1) and (F_2) are constant.

22.4.3 Cool down the combustion tube to about 120°C and introduce a platinum or porcelain boat containing about one gram of accurately weighed ore. After passing dry air through the apparatus for five minutes, connect the absorption tubes and pass dry air at a rate of two bubbles per second. Simultaneously, switch on the furnace and bring the section (E_1) to 800° to 900°C, and the part of the tube containing lead oxides and pumice to 250° to 300°C by (E_2). Maintain the temperatures for 30 minutes, Stop heating without stopping the flow of dry air and disconnect the absorption tubes (F_1) and (F_2), closing their stop-cocks immediately, Allow the tubes to cool to room temperature and weigh after equalizing the pressure by opening the stop-cocks of the tubes momentarily.

22.5 Calculation

$$\text{Combined water, percent} = \frac{A+B}{C} \times 100$$

where

A = increase in weight in g of U-tube (F_1),
B = increase in weight in g of U-tube (F_2), and
C = weight in g of the sample taken.

23. DETERMINATION OF LEAD BY COLORIMETRIC METHODS

23.1 Outline of the Methods – The sample is dissolved in concentrated hydrochloric acid and fumed with sulphuric acid. The insoluble residue containing lead sulphate is filtered off and extracted with ammonium acetate. From this solution, lead is estimated calorimetrically with dithizone or sodium sulphide.

23.2 Reagents

23.2.1 *Concentrated Hydrochloric Acid - see* **6.2.1**.

23.2.2 *Dilute Sulphuric Acid* - 1:1 (by volume).

23.2.3 *Lead-Acid Solution* - Add 50 ml of concentrated sulphuric acid to 800 ml of water with stirring. Dissolve 0.5 g of lead nitrate in 200 ml of water and add slowly to the sulphuric acid solution. Allow to stand overnight and filter the solution through a dense filter paper before use.

23.2.4 *Dithizone Solution* - Dissolve 0.050 g of dithizone in two millilitres of concentrated ammonium hydroxide and 100 ml of water in a separating funnel. Extract with carbon tetrachloride which has been distilled over anhydrous sodium sulphate until the solvent layer is clear bright green. Discard the solvent layer which contains impurities and filter the aqueous portion through an ashless paper. The solution shall be prepared fresh as needed.

23.2.5 *Citric Acid Solution* - 20 percent (*w/v*).

23.2.6 *Concentrated Ammonium Hydroxide* - sp gr 0.90.

23.2.7 *Potassium Cyanide Solution* - 10 percent (*w/v*).

23.2.8 *Standard Lead (Stock) Solution* - Dissolve 0.1600 g of pure lead nitrate in water containing five millilitres of concentrated nitric acid, makeup to 100 ml in a volumetric flask and mix well.

23.2.9 *Standard Lead (Dilute) Solution* (1 *ml* = 0.02 *mg of* Pb) - Transfer five millilitres of standard lead (stock) solution to a 250-ml volumetric flask, make up to the mark with water and mix well. Prepare the solution fresh as required.

23.2.10 *Ethyl Alcohol* - 50 percent.

23.2.11 *Ammonium Acetate* - solid.

23.2.12 *Ammonium Acetate Wash Solution* - Dissolve 10 g of ammonium acetate per litre of water.

23.2.13 *Sodium Sulphide Solution* - 10 percent (*w/v*)

23.2.14 *Carbon Tetrachloride*

23.3 Procedure

23.3.1 Weigh accurately about two grams of the sample, transfer to a 400-ml beaker and digest on a hot-plate or sand-bath with 25 to 30 ml of concentrated hydrochloric acid until the ore is attacked completely. Add 40 ml of dilute sulphuric acid and evaporate the solution until strong fumes of sulphuric acid are evolved: Cool and dilute to about 200 ml with lead-acid solution and boil until all the soluble matter has dissolved. Cool and add about 100 ml of ethyl alcohol solution. Stir and keep overnight.

23.3.2 Filter off the solution through a No. 40 filter paper and wash with lead-acid solution about 10 times, and then with ethyl alcohol solution three to four times to remove the free acid. Discard the filtrate and washings. Transfer the precipitate back to the beaker in which lead was precipitated, using a jet of water (preserve the filter paper). Dilute to 70 to 80 ml with water and add 8 to 10 g of ammonium acetate. Stir and boil for about five minutes. Filter off the solution through the same filter paper and wash six to seven times with hot ammonium acetate wash solution, collecting the filtrate and washings in a 250-ml volumetric flask. Discard the insoluble residue. Cool the filtrate and washings, make up to the mark and mix well.

23.4 Dithizone (Referee) Method - Pipette out 25 to 100 ml (depending on the lead content) of the solution into a 250-ml separating funnel. Add five millilitres each of solutions of citric acid and potassium cyanide. Make ammoniacal, add about five milliliters of dithizone solution and extract with successive 20, 10 and 10 ml portions of carbon tetrachloride solution. Combine the dithizone extracts and make up to 50 ml. Prepare a standard from the standard lead (dilute) solution using the same quantities of the reagents and extracting in the same manner. The quantity of standard lead (dilute) solution taken should be such that the colours match approximately. Compare the intensities of the colours in a suitable type of colorimeter with a closed cell.

23.4.1 *Calculation*

$$\text{Lead, percent} = A \times \frac{H_1}{H_2} \times 0.00002 \times \frac{250}{B} \times \frac{100}{C}$$

where

A = volume in ml of standard lead (dilute) solution,
H_1 = height of column of standard lead (dilute) solution
H_2 = height of column of the solution of the sample,
B = volume in ml of the aliquot sample taken out of 250 ml solution, and
C = weight in g of the sample taken.

23.5 Sodium Sulphide (Alternate) Method - Pipette out a suitable aliquot (depending on the lead content) of the solution obtained in **23.3.2** into a 100-ml Nessler tube. Add five millilitres each of solutions of citric acid and potassium cyanide. Make alkaline with ammonia and add three to four drops of sodium sulphide solution. Stir well and after two to three minutes, compare the colour with that developed with a standard prepared from the standard lead (dilute) solution using the same quantities of reagents. The quantity of standard lead (dilute) solution taken should be such that the colours match approximately. Compare intensities of the colours in a suitable type of colorimeter.

23.5.1 *Calculation - see* **23.4.1**.

24. DETERMINATION OF COPPER BY COLORIMETRIC METHODS

24.1 Outline of the Methods - Copper is precipitated from the hydrochloric acid solution of the sample by passing hydrogen sulphide. The copper sulphide is dissolved in dilute nitric acid. From this solution, copper is determined colorimetrically with sodium diethyl-dithiocarbamate or potassium ferro-cyanide.

24.2 Reagents

24.2.1 *Concentrated Hydrochloric Acid – see* **6.2.1**.

24.2.2 *Hydrofluoric Acid* – 40 percent.

24.2.3 *Dilute Sulphuric Acid* – 1:1 (by volume).

24.2.4 *Hydrogen Sulphide* – gas.

24.2.5 *Hydrogen Sulphide Wash Solution* – Saturate dilute hydrochloric acid (1:99) with hydrogen sulphide.

24.2.6 *Dilute Nitric Acid* – 1:2 (by volume).

24.2.7 *Potassium Bisulphate* – solid.

24.2.8 *Concentrated Ammonium Hydroxide* – sp gr 0.90.

24.2.9 *Sodium Sulphate* – anhydrous.

24.2.10 *Sodium Diethyl-dithiocarbamate Solution* – 0.1 percent (*w/v*).

24.2.11 *Carbon Tetrachloride*

24.2.12 *Ammonium Nitrate Solution* – 10 percent (*w/v*).

24.2.13 *Citric Acid Solution* – 20 percent (*w/v*).

24.2.14 *Potassium Ferrocyanide Solution* – four percent (*w/v*).

24.2.15 *Standard Copper (Stock) Solution* – Dissolve 0.3928 g of pure copper sulphate crystals in water containing one to two millilitres of dilute sulphuric acid (1:1) an d make up to 100 ml in a volumetric flask.

24.2.16 *Standard Copper (Dilute) Solution* (1 *ml* = 0.02 *mg of* Cu) – Transfer five millilitres of the stock solution to a 250-ml volumetric flask and dilute to the mark with water and mix well. Prepare fresh when required.

24.2.17 *Ammonium Hydroxide Wash Solution* – 1:20 (by volume).

24.3 Procedure

24.3.1 Weigh accurately about two grams of the sample and transfer to a 400-ml beaker. Digest in 25 to 30 ml of concentrated hydrochloric acid until the ore is completely attacked. Dilute to about 80 to 100 ml with water and boil for three to four minutes. Filter the solution through .a No. 41 filter paper and wash the insoluble residue five to six times with hot water. Preserve the filtrate.

24.3.2 Ignite the insoluble residue in a platinum crucible at about 600°C until all the carbon is burnt off. Treat the residue with two to three drops of dilute sulphuric acid solution and 6 to 7 ml of hydrofluoric acid. Evaporate to dryness and ignite the residue at 600°C for five minutes. Fuse the residue in the crucible with two grams of potassium bisulphate for about 10 to 15 minutes and extract the cooled fused mass in 70 to 80 ml of water containing five millilitres of concentrated hydrochloric acid. Boil until the fused mass is completely disintegrated. Wash in the crucible and lid. If any insoluble residue is left, filter the solution through a No. 40 filter paper and wash the insoluble residue five to six times with hot water. Combine this filtrate and washings with those preserved under **24.3.1** and concentrate to about 250 ml.

24.3.3 Neutralize the solution with concentrated ammonium hydroxide until a persistent precipitate is formed. Redissolve the precipitate in the minimum amount of concentrated hydrochloric acid and add 12 ml in excess. Pass hydrogen sulphide gas for about half an hour and keep for another half an hour at 50° to 60°C. Filter through a No. 41 filter paper and wash eight to ten times with hydrogen sulphide wash solution. Preserve the filtrate for determination of zinc (*see* **25.3.1**)

24.3.4 Transfer the filter paper with the precipitate to the same beaker in which copper was precipitated. Add 30 to 40 ml of dilute nitric acid and digest on the hot-plate for 15 to 20 minutes. Dilute to 70 to 80 ml with hot water and make distinctly ammoniacal. Keep just boiling for three to four minutes and filter through a No. 40 filter paper into a 250-ml volumetric flask. Wash with hot dilute ammonium hydroxide wash solution six to seven times. Discard the residue. Cool the solution and make up to the mark and mix well.

24.4 Diethyl-dithiocarbamate (Referee) Method - Pipette out a suitable aliquot (depending on copper content) of the solution (*see* **24.3.4**) into a separating funnel. Make distinctly ammoniacal. Add 10 ml of citric acid solution, Add 10 ml of sodium diethyl-dithiocarbamate and extract successively with 10 ml, 5 ml and 5 ml of carbon tetrachloride respectively. Combine the carbon tetrachloride extracts and make up to 25 ml. Add a little anhydrous sodium sulphate to, clear the solution. Prepare a standard from the standard copper (dilute) solution, using the same quantities of the reagents and extracting in the same manner. The quantity of standard copper (dilute) solution taken should be such that the colours match approximately. Compare the intensities of the colours in a suitable type of colorimeter.

24.4.1 *Calculation*

$$\text{Copper, percent} = A \times \frac{H_1}{H_2} \times 0.00002 \times \frac{250}{B} \times \frac{100}{C}$$

where

A = volume in ml of standard copper (dilute) solution taken,
H_1 = height of column of standard copper (dilute) solution,
H_2 = height of column of the solution of sample,
B = volume in ml of the aliquot taken out or 250 ml solution, and
C = weight in g of the sample taken.

24.5 Ferrocyanide (Alternate) Method – Pipette out a suitable aliquot (depending on copper content) of the solution obtained in **24.3.4** into a 250-ml beaker. Boil to expel all ammonia and add one drop of dilute nitric acid. Transfer to a 100-ml Nessler tube. Add solutions of five millilitres of ammonium nitrate and one millilitre of potassium ferrocyanide. After keeping for two to three minutes, compare the colour developed with that obtained by a definite volume of standard copper (dilute) solution to which the same reagents are added. The quantity of standard copper (dilute) solution taken should be such that the colours match approximately. Compare the intensities of colours in a suitable type of colorimeter.

24.5.1 *Calculation* - *see* **24.4.1**.

25. DETERMINATION OF ZINC BY THE DITHIZONE (COLORIMETRIC) METHOD

25.1 Outline of the Method - In the filtrate, from copper estimation, zinc is precipitated as sulphide in a weakly acidic ammonium formate buffer medium. The sulphide is dissolved in dilute hydrochloric acid and any small amounts of iron occluded are removed as hydroxide. From the filtrate, zinc is estimated calorimetrically with dithizone which forms a red coloured keto complex.

25.2 Reagents

25.2.1 *Tartaric Acid* - solid.

25.2.2 *Formic Acid Mixture* - Add 200 ml of formic acid to 770 ml of water and add to this 30 ml of concentrated ammonium hydroxide.

25.2.3 *Hydrogen Sulphide* - gas.

25.2.4 *Formic Acid Wash Solution* - Dilute 25 ml of formic acid mixture (*see* **25.2.2**) to one litre and pass hydrogen sulphide.

25.2.5 *Ammonium Chloride* - solid.

25.2.6 *Concentrated Ammonium Hydroxide* - sp gr 0.90.

25.2.7 *Dithizone Solution* - *see* **23.2.4**.

25.2.8 *Carbon Tetrachloride*

25.2.9 *Citric Acid* - solid.

25.2.10 *Dilute Hydrochloric Acid* - 1:10 (by volume)

25.2.11 *Ammonium Hydroxide Wash Solution* - Add five millilitres of concentrated ammonium hydroxide to one litre of water and dissolve in this solution two grams of ammonium chloride.

25.2.12 *Standard Zinc (Stock) Solution* - Dissolve 0.5000 g of pure zinc in 10 ml of concentrated hydrochloric acid and 20 ml of water. Cool, transfer to a one-litre volumetric flask, make up to the mark and mix well.

25.2.13 *Standard Zinc (Dilute) Solution* (1 *ml* = 0.01 *mg of* Zn) - Dilute five millilitres of the stock solution (*see* **25.2.12**) to 250 ml in a volumetric flask, and mix well. Prepare fresh when required.

25.3 Procedure

25.3.1 Boil off hydrogen sulphide from the filtrate reserved in **24.3.3**. Concentrate the solution to 200 ml. Add 7 to 8 g of tartaric acid and neutralize carefully with concentrated ammonium hydroxide until there is a very faint smell of ammonia. Boil to drive off excess of ammonia and add 25 ml of formic acid mixture. Heat again to boiling and pass a rapid stream of hydrogen sulphide for 20 minutes, keeping the solution just below boiling. Add a little paper pulp and immediately filter through a No. 42 filter paper and wash seven to eight times with cold formic acid wash solution. Dissolve the precipitate on the filter paper with hot dilute hydrochloric acid, collecting the solution into the same beaker in which zinc was precipitated.

25.3.2 Dilute the solution to 100 ml, boil to expel hydrogen sulphide and add 5 to 6 g of ammonium chloride. Make just ammoniacal with concentrated ammonium hydroxide and boil for two to three minutes. Filter off any iron hydroxide separated through a No. 41 filter paper and wash with warm ammonium hydroxide wash solution six to seven times, collecting the filtrate and washings in a 250-ml volumetric flask. Discard the precipitate. Cool the solution, make up to the mark and mix well.

25.3.3 Pipette out a suitable aliquot of the solution (depending on the zinc content) into a separating funnel. Add 0.5 g of citric acid and adjust the *p*H to 8.0 to 9.2. Add three to five millilitres of dithizone solution and extract successively with 10 ml, 5 ml and 5 ml of carbon tetrachloride respectively. Collect the carbon tetrachloride extracts and make up to 25 ml. Prepare a standard from standard zinc (dilute) solution using the same quantities of reagents and extracting in the same manner. The quantity of standard zinc (dilute) solution taken should be such that the colours match approximately. Compare the intensities of the colours in a suitable type of calorimeter.

25.4 Calculation

$$\text{Zinc, percent} = A \times \frac{H_1}{H_2} \times 0.00001 \times \frac{250}{B} \times \frac{100}{C}$$

where

A = volume in ml of standard zinc (dilute) solution taken,
H_1 = height of column of standard zinc (dilute) solution,
H_2 = height of the column of the solution of the sample,
B = volume in ml of the aliquot taken out of 25 ml solution, and
C = weight in g of the sample taken.

26. DETERIMINATION OF ARSENIC BY THE GUTZEIT METHOD

26.1 Outline of the Method - A sulphuric acid solution of the sample is prepared after oxidizing all arsenic with bromine. From this solution, arsenic is estimated by the usual Gutzeit method.

26.2 Apparatus - The apparatus consists of the following parts which are shown assembled in Fig. 3.

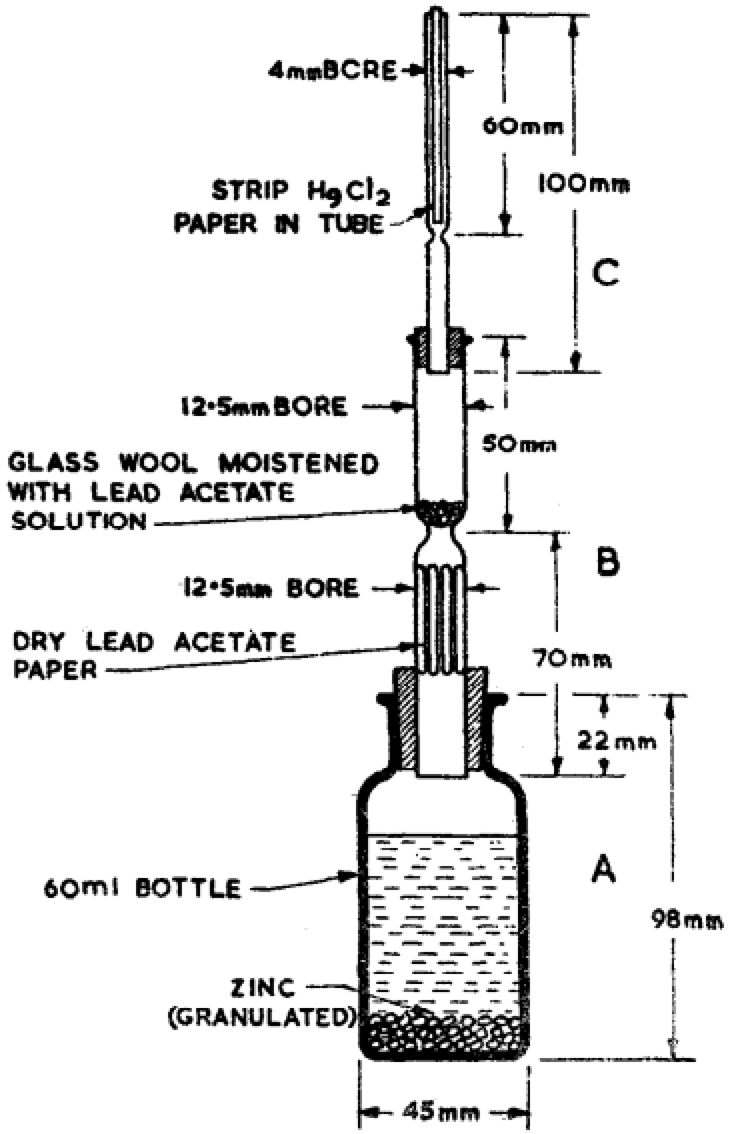

FIG. 3 GUTZEIT APPARATUS FOR DETERMINATION OF ARSENIC

26.2.1 *Gutzeit Bottle* - wide-mouthed bottle *A*, capacity of 60 ml.

26.2.2 *Tube B* - made of Pyrex glass, 120 × 12.5 mm, with a constriction at a distance of 50 mm from the upper end.

26.2.3 *Tube C* - made of Pyrex glass, 100 × 4 mm, with a constriction at a distance of 60 mm from the upper end.

26.2.4 *Rubber Stoppers* - two; one to fit the Gutzeit bottle and bored with a hole to take the wider tube, and the other to fit inside the wider tube and bored with one hole to take the narrower tube.

26.3 Reagents

26.3.1 *Concentrated Hydrochloric Acid - see* **6.2.1**.

26.3.2 *Concentrated Nitric Acid - see* **6.2.7**.

26.3.3 *Dilute, Sulphuric Acid* - 1:1 (by volume).

26.3.4 *Bromine Solution* - Dissolve two parts of liquid bromine in three parts of carbon tetrachloride.

26.3.5 *Lead Acetate Paper* - Soak sheets of No. 1 fitter paper in one percent (*w/v*) solution of lead acetate $[Pb(C_2H_3O_2)_2, 3H_2O]$ in water (containing just enough of acetic acid to clear the solution) and dry them. Cut the sheets into strips of 70 × 50 mm.

26.3.6 *Sensitized Mercuric Chloride Paper* - Cut No. 1 filter paper sheets (50 × 50 cm) in four equal squares and dip them into mercuric chloride solution (0.35 percent *w/v*). The paper should be of uniform thickness, otherwise irregularity in the length of the stain, for the same amount of arsenic, may occur. Hang the squares and dry them in air, free from gas fumes, hydrogen sulphide being particularly undesirable. When dry, trim off about one centimeter of the outer edge and cut the squares into strips, 70 × 2.5 mm each. Preserve the papers in bottles with air-tight stoppers. Paper with a white deposit of mercuric chloride should be rejected. Stains shall be made with each batch of paper.

26.3.7 *Potassium Iodide* - solid.

26.3.8 *Zinc* - granulated, arsenic-free.

26.3.9 *Stannous Chloride solution* $(SnCl_2, 2H_2O)$ - Dissolve 40 g of arsenic-free stannous chloride in 60 ml of concentrated hydrochloric acid and 40 ml of water by warming.

26.3.10 *Standard Arsenic Trioxide (Stock) Solution* - Dissolve 0.1320 g of arsenic trioxide in 50 ml of concentrated hydrochloric acid. Transfer to a 100-ml volumetric flask, make up to the mark and mix well with water.

26.3.11 *Standard Arsenic Trioxide (Dilute) Solution* (1 *ml* = 0.01 *mg of* As) - Dilute five millilitres of the stock solution (*see* **26.3.10**) to 500 ml in a volumetric flask, and mix well. Prepare fresh when required.

26.3.12 *Hydrofluoric Acid* - 40 percent.

26.3.13 *Potassium Bisulphate* - solid.

26.3.14 *Standard Stains* - Make the standard stains on the sensitized mercuric chloride paper (see **26.3.6**) with the appropriate quantities of standard arsenic trioxide (dilute) solution. For the preparation of the stains, place the requisite amount of the standard arsenic trioxide (dilute) solution in the Gutzeit bottle with the amounts of reagents prescribed for the regular test and make the run exactly as described for the procedure under **26.4**.

26.3.14.1 *Preservation of stains* - Dip the strips of sensitized mercuric chloride paper with the standard arsenic stains (*see* **26.3.14**) in molten paraffin (free from water) and mount on a sheet of white paper folded back to form a cylinder. Place the cylinder thus formed in a glass test tube containing phosphorus pentoxide, and close it with a stopper. Keep the stained strips dry, otherwise the stains soon fade, hence perfectly dry the glass test-tube and the paper on which the strips are mounted. While not in use, keep the test-tube in an empty cardboard box, as light will gradually fade the colour of the stains. Fresh stains should be prepared periodically and a stain suspected to have faded shall not be used. Fresh stains shall he prepared in case of dispute.

26.4 Procedure

26.4.1 Weigh accurately about two grams of the sample into a 400-ml beaker and add five millilitres of bromine solution. Keep for 15 minutes, and digest in a mixture of 20 ml of concentrated hydrochloric acid and 10 ml of concentrated nitric acid. After the ore is completely attacked, add 30 ml of dilute sulphuric acid and evaporate to fumes of sulphuric acid. Cool and add 70 to 80 ml of water. Boil until the soluble salts have dissolved. Filter the solution through a No. 41 filter paper and wash with hot water five to six times. Preserve the filtrate.

26.4.2 Ignite the insoluble residue in a platinum crucible at about 500 C until all carbon is burnt off. Cool and treat the residue with two to three drops of dilute sulphuric acid solution and 6 to 7 ml of hydrofluoric acid. Evaporate to dryness and fuse the residue with two grams of potassium bisulphate for 10 minutes. Cool and extract the fused mass in 60 to 70 ml of water containing 10 ml of dilute sulphuric acid. Wash in the crucible and lid and combine the solution with the filtrate preserved in **26.4.1**. Concentrate the solution and make up to 100 ml in a volumetric flask and mix well.

26.4.3 Transfer a suitable aliquot of the solution, containing 0.01 to 0.05 mg of arsenic, to the Gutzeit bottle. The aliquot should contain 5 to 6 ml of concentrated sulphuric acid. If the acidity is less, add more dilute sulphuric acid to bring it to the above strength. Add 0.5 ml of stannous chloride solution followed by one gram of potassium iodide. Dilute to about 40 ml with water and add five grams of granulated zinc and immediately connect the apparatus as shown in Fig. 3. The temperature of the contents should be kept at 20° to 25°C and the reaction allowed to proceed for one hour. At the end of this period, the apparatus is disconnected, the mercuric chloride paper is removed and the stain compared with the standard stains preserved under **26.3.14.1**.

26.5 Calculation

$$\text{Arsenic, percent} = \frac{A}{1000} \times \frac{100}{B} \times \frac{100}{C}$$

where

A = weight in mg of arsenic in the standard stain,

B = volume in ml of the solution of the sample taken out of 100 ml, and

C = weight in g of the sample taken.