IS 1559 PARTS 8, 9, 10, 11:2022

WORKING DRAFT

Indian Standard For Methods Of Chemical Analysis Of Silicomanganese (IS 1470:2013), Ferrophosphorus (IS 1471:1988), Ferrovanadium (IS 1466:1985), and Ferrotungsten

FOREWORD

This Indian Standard was initially formulated in 1961 specifying the methods for chemical analysis of ferrosilicon, ferromanganese and speigeleisen, silicomanganese, ferromolybdenum, ferrophosphorus, ferrotitanium, ferrovanadium and ferrotungsten.

The standard has now been revised to

a) Remove the methods for chemical analysis of the following ferroalloys for which other standards are available
- IS 1559 (Parts 1 to 7):1982 - Methods for chemical analysis of ferrosilicon
- IS 13452:2019 - Methods for chemical analysis of ferrochromium
- IS 13938 Part (1,3,4):1994 - Methods for chemical analysis of ferromanganese
- IS 12614 (Parts 1 to 7):1988 - Methods for chemical analysis of Ferromolybdenum
- IS 13840:2019 - Methods for chemical analysis of ferrotitanium

b) Split IS 1559:1961 into four new standards: **IS 1559 PARTS 8, 9, 10, 11:2022** specifying the methods for analysis of Silicomanganese (IS 1470:2013), Ferrophosphorus (IS 1471:1988), Ferrovanadium (IS 1466:1985), and Ferrotungsten (IS 1467:1993), respectively retaining the existing methods but also introducing the instrumental methods (ICP-OES) developed by the CSIR-NML for determination of V, Mn, Si ,Al & P in Ferrovanadium (*this may be finalized after due validation procedure)*

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

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 : 2-1960 Rules for Rounding Off Numerical Values (Revised).

IS 1559 PART 8:2022

Methods of analysis of Silicomanganese

1.1 DETERMINATION OF SILICON BY THE GRAVIMETRIC METHOD

1. Outline of the Method – The sample is fused with sodium peroxide and the fused mass evaporated with hydrochloric acid, baked and then estimated by hydrofluorization.

2. Apparatus – 50-ml iron crucible.

Reagents-

Sodium Hydroxide, Solid

2.1.3.2 Dilute Hydrochloric Acid 1:1 and 1:20 (v/v)

2.1.3.3 Conc. Hydrochloric acid – sp gr 1.16 (see IS 265)

2.1.5 Hydrofluoric Acid – 40%

2.1.3 Procedure

2.1.3.1 Weigh accurately 0.5 g of the sample and transfer to a 50-ml iron crucible. Add approximately about 10 g of sodium peroxide and mix the contents thoroughly with a small iron or nickel rod. Cover the mixture with a layer of about 2 g additional sodium peroxide.

2.1.3.2 Carry out baking as follows: Extract the melt with minimum quantity of hot water in a porcelain dish, washing the crucible and the lid with a jet of hot water. Acidify with dilute hydrochloric acid and add about 50 ml excess. Evaporate to dryness and bake for one hour at 100 to 110°C. Re-dissolve the mass in 40 ml of conc. Hydrochloric acid by warming and dilute with 50 ml water. Raise to boil, alow to settle slightly and filter through filter paper no. 40. Wash 10-12 times alternately with hot dilute hydrochloric acid (1:20) and hot water. Finally rinse with hot water till the washings are free from chlorides. Preserve the paper and the residue. Evaporate the filtrate and washings to dryness and repeat the process of baking, washing etc as above.

2.1.3.3 Reserve the filtrate for estimation of manganese by the Bismuthate and Volhard methods (see 2.2 and 2.3).

2.1.3.4 Complete the estimation of silicon as given under

2.1.3.4.1 Place the papers and the residue from 2.1.3.2 in the platinum crucible and dry completely on a hot plate. Heat the crucible in a muffle furnace at 1000°C for about 30 minutes, cool in a dessicator and weigh. Ignite again for 10 minutes at the above temperature as a check for constant weight.

2.1.3.4.2 Add sufficient dilute sulphuric acid to moisten the residue, then add carefully about 10 ml of hydrofluoric acid and cautiously evaporate to dryness. Ignite over a free flame to constant weight. Record the loss in weight which represents the silica. (Note: A blank determination should be carried out when the silica content of the ferro-alloy is less than 10%)

2.1.3.4.3 Calculation

Silicon percent = (A X 46.72)/B

Where

A = weight in g of silica obtained

B = weight in g of sample taken

2.2 DETERMINATION OF MANGANESE BY THE BISMUTHATE METHOD

2.2.1 Outline of the Method – Bivalent manganese in the filtrate from silicon determination is oxidized to permanganic acid by the use of sodium bismuthate. Manganese is then estimated by the use of ferrous sulphate and potassium permanganate solutions.

2.2.2 Reagents –

2.2.2.1 – Dilute nitric acid 3:97 (v/v)

2.2.2.2 - Concentrated sulphuric acid – sp gr 1.84 (See IS 265)

2.2.2.3 - Sulphurous acid solution – make 5% (approx.) solution of Sulphur dioxide in water. Prepare fresh as needed.

2.2.2.4 – Sodium bismuthate – 80% solution and solid

2.2.2.5 – Ferrous Ammonium sulphate solution – 0.1 N approx. (dissolve 39.2 g of ferrous ammonium sulphate crystals ($FeSO_4$, $(NH_4)2SO_4$,$6H_20$) in cold dilute sulphuric acid (5:95) and make up to one litre with this acid. Mix well and keep in an amber coloured, glass stoppered bottle)

2.2.2.6 – Phosphoric Acid – 85%

2.2.2.7 – Standard potassium permanganate solution – 0.1 N, (Dissolve 3.2 g of potassium permanganate in one litre of water. Let stand in the dark for 2 weeks and filter without washing through a Gooch crucible or fritted glass crucible of fine porosity avoiding contact with rubber or other organic material. Store in a dark coloured glass stoppered bottle. Standardize against Analar sodium oxalate by weighing 0.134 g of salt, dissolving in 250 ml of dilute sulphuric acid (5:95) and titrating against the permangnate

2.2.3 Procedure

2.2.3.1 Take the solution reserved under 24.4.1 and evaporate with 10 ml of concentrated sulphuric acid to fumes. Cool, dilute to 100 ml cautiously and boil until all the salts are dissolved. Transfer to a 500 ml flask and make up to the mark. Use suitable aliquots for determination of manganese by the Bismuthate or Volhard methods.

2.2.3.2 Pipette out exactly 25 ml of the solution (or such portion that will contain 0.03 g of manganese) into a 500-ml beaker. Add about 50 ml of concentrated nitric acid, heat to boiling, remove from the heat and add sodium bismuthate a little at a time until a precipitate of manganese dioxide has formed. When this occurs add sulphurous acid dropwise until the precipitate dissolves. Boil the solution for about 5 minutes to completely expel oxides of nitrogen and cool to 10 to 15 °C.

2.2.3.3 To the cold solution add about 1 to 2 g of sodium bismuthate and agitate briskly for one minute; filter immediately through a Gooch crucible. Wash with cold dilute nitric acid until the washings are colourless. Reject the insoluble residue. The temperature of the filtrate shall be maintained between 10 to 15 °C. To the filtrate, add a measured excess of ferrous ammonium sulphate solution (50 ml) and stir. Add 2 ml of syrupy phosphoric acid and immediately titrate with standard potassium permanganate solution until a faint and permanent pink colour appears.

2.2.3.4 Carry out a blank determination through all stages using the same amount of ferrous ammonium sulphate and phosphoric acid titrate with standard permanganate solution. Manganese to be calculated as follows

Manganese, percent = $((A-B)C \times 1.10)/D$

Where

A= volume in ml of the standard permanganate solution required to titrate the blank

B= volume in ml of the standard permanganate solution required to titrate the excess ferrous ammonium sulphate

C= normality of the standard permanganate solution

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

2.3 DETERMINATION OF MANGANESE BY THE VOLHARD (ALTERNATE) METHOD

2.3.1 Outline of the method: Iron hydroxide in the filtrate from silicon determination is precipitated by means of zinc oxide and filtered. Bivalent manganese in the filtrate is determined by its oxidation to the quadrivalent state with standard permanganate solution

2.3.2 Reagents

2.3.2.1 Concentrated sulphuric acid, sp gr 1.84 (See IS 265)

2.3.2.2 Sodium carbonate solution – dissolve 318 g of anhydrous sodium carbonate in water and make up to one litre

2.3.2.3 Zinc oxide emulsion – make a suspension of finely divided zinc oxide by thoroughly shaking 50 g of the reagent in 300 ml of water

2.3.2.4 concentrated nitric acid – sp gr 1.42 (see IS 264)

2.3.2.5 Standard potassium permanganate solution

2.3.1.2 Pipette out 25 ml of the solution prepared under 2.2.3.1 (for lower percentages a suitable aliquot may be taken) into a 500 ml conical flask. Add in small amounts zinc oxide emulsion until a point is reached where the liquid suddenly coagulates. Dilute the contents to 200 ml; boil and add 2 to 3 drops of concentrated nitric acid and titrate against standard potassium permanganate solution.

2.3.1.3 The permanganate causes a precipitate which clouds the liquid and it is therefore necessary to titrate cautiously and agitate the flask after each addition and then allow the precipitate to settle sufficiently to observe whether or not the solution is coloured pink (When the supernatant liquid shows persistent pink tinge, bring the contents of the flask nearly to a boil once more and again observe if the pink still persists, adding permanganate solution, if necessary). When the colour is permanent, the end point is reached. Three separate titrations shall be made, the first two to get pilot reading so that in the final titration all the permanganate required can be added as rapidly as possible and the colour observed.

Manganese, percent = $AB \times 1.666/C$

Where

A= volume in ml of standard permanganate solution consumed

B= normality of standard permanganate solution

C=weight in g of the sample represented by the aliquot used

2.4 DETERMINATION OF CARBON (TOTAL) BY THE DIRECT COMBUSTION GRAVIMETRIC METHOD

2.4.1. Outline of the method – The sample is burnt in a stream of pure oxygen and the resulting carbon dioxide is absorbed in soda asbestos after removal of the contaminants. The increase in weight of the absorbent is proportional to the carbon content of the sample.

2.4.2 Apparatus – Assembly of the apparatus is shown at Fig. 1

Source of oxygen supply – gas holder A (capacity 8 to 10 litres) containing 99.5% percent oxygen free from carbonaceous matter, connected by rubber tubing with the gas purifying train. The gas holder should be filled up before starting the operation.

Oxygen purification train – Consists of Arnold bottles (B) and (C), the latter containing concentrated sulphuric acid the exit bulb of which is packed with glass wool and another absorption bottle (D) containing soda asbestos which passes through IS sieve 140 but is retained on IS sieve 50 and ‘anhydrone’ in layers connected in series between the gas holder and the inlet end of the combustion tube. A layer of about 12 mm in anyhdrone is placed on top for removing the moisture in the gas and the soda asbestos removes carbon dioxide in the gas.

Furnace – A horizontal furnace tube (E) heated to 1350°C by electricity

Combustion tube – A combustion tube of approx. 650 mm long and 20 mm inner diameter made of fused silica, fireclay or any other suitable material should be used. In the exit end of the tube an ignited asbestos plug 75 mm long is placed to lightly retain ferric oxide carried over by the gas stream

Absorption train – Consists of an Arnold bottle (F) to prevent back suction, a gas absorption bottle (G) filled with chromic anhydride in dilute sulphuric acid 2:1 (v/v) to remove oxides of sulphur from the gas stream, a bottle (H) containing about 40 ml of concentrated sulphuric acid to remove most of the moisture from exit gas, the exit end of this bottle is filled with glass wool to remove sulphuric acid mist, one tube (J) containing 'anhydrone' or any other suitable dessicant and carbon dioxide absorption bottle (K) (80 ml capacity) containing a layer of soda asbestos or ascarite, which should be uniformly graded and evenly packed with a layer of anhydrone on top, all connected in series with the exit end of the combustion furnace and the atmosphere. The filings in (K) are held in position by small plugs of glass wool. A bottle (L) packed similarly to bottle (K) acts as guard against atmospheric gases. Its exit end is attached to a flow meter. Bottles (F), (G), and (H) may be replaced with a Midvale or Nesbitt bulb (N) containing precipitated manganese dioxide over ignited asbestos.

2.4.3. Reagents

Concentrated sulphuric acid

Dilute sulphuric acid

Chromic-sulphuric acid solution. – Saturate 100 ml of dilute sulphuric acid (2:1) with chromic anhydride

Manganese sulphate – solid

Concentrated ammonium hydroxide – sp gr 0.90

Ammonium persulphate solution – 25 and 22.5 percent (v/v)

Precipitated Manganese Dioxide –

a) Dissolve 200 g of Manganese Sulphate in 2500 ml of water, add concentrated ammonium hydroxide until ammoniacal, followed by 1000 ml of freshly prepared ammonium persulphate solution (22.5 percent) and heat to boiling. Boil for 10 minutes, adding more concentrated ammonium hydroxide to maintain the ammoniacal condition. Further addition of solutions of ammonium persulphate and ammonium hydroxide may be required until precipitation is judged to be complete.

b) Discontinue boiling and allow the precipitate to settle, wash by decantation 6 to 8 times and 500 ml to 600 ml portions of water, allowing the precipitate to settle completely between washings. Finally wash 2 to 3 times by decantation with 500 ml to 600 ml portions of dilute sulphuric acid. Transfer the precipitate to a Buchner funnel and wash with hot water until free from sulphates. Dry the residue and 105 to 110°C

Soda Asbestos – It should be graded to IS sieves 140 to 50 (aperture 1405 to 500 microns)

Anhydrone or magnesium perchlorate

Lead foil – of assay grade and 0.127 mm in thickness

Magnesite brick powder – which has passed through IS sieve 50 (aperture 500 micron) shall be used for spreading in the boat on which the sample is to be placed before combustion. This powder shall be calcined

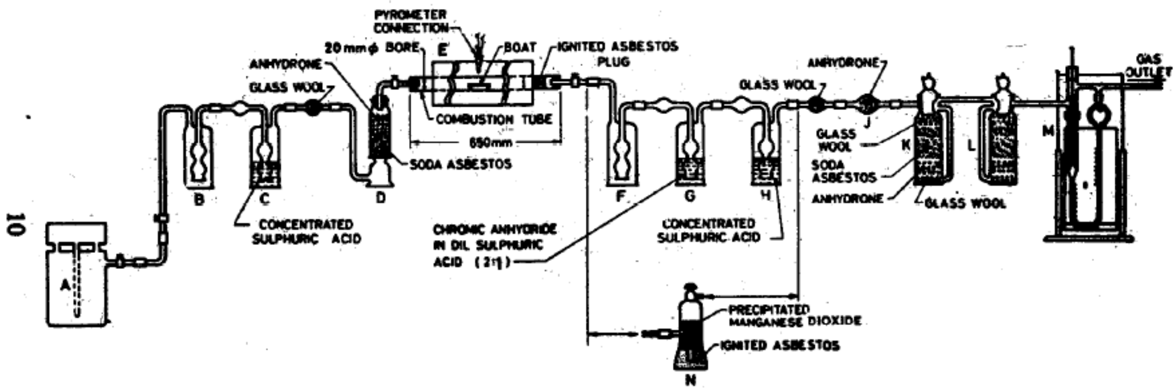


Fig. 1 Apparatus for Determination of Carbon (Total) by the Direct Combustion (Gravimetric) Method

2.4.4. Procedure

Heat the furnace to a temperature between 1200 to 1300°C. Check for leaks. Pass a slow stream of oxygen for about 15 minutes through the whole train of the apparatus and then weigh the carbon dioxide absorption tube. A counterpoise of a similar bottle is recommended in a balance for weighing. After taking the first weight connect in back to the apparatus, pass oxygen for 15 minutes and weigh again. If constant weight is obtained, the apparatus is ready to use.

Weigh one gram of the sample mixed with 2.0 g of a low carbon standard steel of known carbon content and place in a previously ignited combustion boat made of either porcelain, refractory, clay, nickel sheet or alumina and of dimensions about 100 x 20 x 15 mm with walls as thin as possible and cover the sample with lead foil (1.5 g twice folded), Before placing the sample in the boat sprinkle in the bottom of the boat some burnt magnesite brick dust which has been tested by the blank run. Insert the boat quickly into the heat zone of the furnace, with the rubber stopper replaced at the end of the combustion tube, wait for about a minute so that the boat attains the temperature of the furnace and pass a rapid stream (300 to 500 ml per minute) of oxygen for 10-15 minutes to sweep out carbon dioxide. At the end of this period, remove the carbon dioxide absorption bulb, cool in a dessicator and weigh quickly against a similar tube used as a counterpoise. This increase in weight represents carbon dioxide.

Carry out a blank determination on 2.0 g of the same low carbon standard steel that was mixed with the sample.

Carbon, percent = (A-B) x 27.29/C

Where

A= weight in g of carbon dioxide absorption tube after test

B = weight in g of carbon dioxide absorption tube after in blank

C = weight in g of sample taken

DETERMINATION OF CARBON (TOTAL) BY THE DIRECT COMBUSTION VOLUMETRIC (ALTERNATE) METHOD

Determine carbon content of the sample by following the procedure given under 8. [REPRODUCE HERE THE PROCEDURE GIVEN IN 8 OF IS 1559:1961]

DETERMINATION OF PHOSPHORUS BY THE ALKALIMETRIC METHOD

Determine phosphorus content of the sample by following the procedure as given under 22 with the following modification.

Transfer the sample to a large platinum dish provided with a cover and add 50 ml of concentrated nitric acid and then 10 to 15 ml hydrofluoric acid in small amounts. Complete the estimation as under 23.3.1 and 23.3.2. [REPRODUCE HERE THE PROCEDURE GIVEN IN 23.3.1 and 23.3.2 OF IS 1559:1961]

DETERMINATION OF SULPHUR BY THE GRAVIMETRIC METHOD

Determine sulphur content of the sample by following the procedure as given under 9. . [REPRODUCE HERE THE PROCEDURE GIVEN IN 9 OF IS 1559:1961]

IS 1559 PART 9:2022

METHODS OF ANALYSIS OF MOLYBDENUM

DETERMINATION OF MOLYBDENUM BY THE PERMANGANATE TITRATION METHOD

Outline of the Method - After the removal of silica and iron, the latter having been removed by repeated precipitation, molybdenum is separated from the ammoniacal filtrate by treatment with hydrogen sulphide in presence of tartaric acid and reduced in a Jones reductor provided with ferric sulphate solution in the receiver. The reduced solution is then titrated with standard potassium permanganate solution in presence of phosphoric acid.

Ignite the precipitate in a 30-ml platinum crucible at 500 to 600°C and fuse the residue with 2 to 3g of sodium carbonate, cool and dissolve the cold melt in 50 ml of hot water. Filter and wash the residue with warm water. Acidify the filtrate with concentrated hydrochloric acid and add 2 ml in excess; cool to 15 to 20° C, add a little ashless paper pulp and sufficient amount (2 to 5 ml) of a - benzoinoxime solution to precipitate molybdenum. Stir well and filter through filter paper No. 540 and wash with cold a - benzoinoxiine wash solution. Complete the estimation as described under 9.3.3 to 9.3.4. [REPRODUCE HERE THE PROCEDURE GIVEN IN 9.3.3 to 9.3.4 OF IS 1559:1961]

SECTION VI FERROPHOSPHORUS

DETERMINATION OF PHOSPHORUS BY THE MOLYBDATE-MAGNESIA (GRAVIMETRIC) METHOD

Outline of the Method - After the decomposition of the sample by fusion with sodium peroxide, phosphorus is precipitated from the warm acid solution as ammonium phosphomolybdate, dissolved in ammonia, re-precipitated as magnesium-ammonium phosphate which is finally ignited and weighed as magnesium pyrophosphate.

36.2 Reagents

36.2.1 Sodium Peroxide - solid.

36.2.2 Dilute Nitric Acid - 1 : 99 (v/v).

36.2.3 Potassium Permanganate Solution - 25 g per litre (w/v).

36.2.4 Sulphurous Acid- Saturate water with sulphur dioxide gas. Prepare fresh as needed.

36.2.5 Concentrated Ammonium Hydroxide - sp gr 0.90.

36.2.6 Concentrated Nitric Acid - see 6.3.1.

36.2.7 Ammonium Molybdate Solution - see 10.2.10

36.2.8 Dilute Ammonium Hydroxide - 1 : 1 and 1 : 20 (v/v

36.2.9 Citric Acid - solid.

36.2.10 Concentrated Hydrochloric Acid -

36.2.11 Magnesia Mixture - Dissolve 130 g of magnesium sulphate ($Mg SO_4, 7H_2O$) and 75 g of ammonium sulphate in 500 ml of water. Add concentrated ammonium hydroxide in slight excess and let stand overnight. Filter, if necessary and make the solution just acidic by adding a very slight excess of concentrated sulphuric acid, dilute to one litre and keep in a glass-stoppered bottle.

36.3 Procedure

36.3.1 Transfer one gram of finely powdered and accurately weighed sample to an iron crucible and mix with 15 g of sodium peroxide. Spread a thin layer of sodium peroxide on the top of the mixture, cover the crucible with iron lid and fuse the contents by heating first at low temperature and then gradually raising the temperature until complete fusion takes place. Rotate the crucible sufficiently to attack any undissolved particle of the alloy sticking along the sides of the crucible and stir up the fused mass. Keep the contents of the crucible in a molten state for about five minutes, then heat to bright redness for a minute and allow to cool.

36.3.2 Place the crucible in a covered beaker containing about 300 ml of water. Warm for few minutes, remove the crucible and wash it well with warm dilute nitric acid. Neutralize the solution by slowly adding dilute nitric acid and add 40 ml in excess and digest until the solution clears. Filter the solution through a tight paper in a 500-ml volumetric flask and wash the residue with warm dilute nitric acid. Cool to 20° C, dilute to exactly 500 ml, mix well and pipette out an aliquot of 100 ml into a 40 Q-ml beaker.

36.3.3 Add 20 ml of dilute nitric acid and 5 to 10 ml of potassium permanganate solution, and carefully boil until manganese is precipitated. If no precipitate appears, add more potassium permanganate solution and boil again. Dissolve the precipitate by adding sulphurous acid dropwise and boil for two minutes. Add a few milliliters more of sulphurous acid and boil off excess sulphurous acid and neutralize the solution with concentrated ammonium hydroxide until a slight precipitate appears. Redissolve the precipitate by the continuous addition of few drops of concentrated nitric acid, add 4 to 5 ml in excess and heat to 70 to 80°C. Add with stirring 80 ml of ammonium molybdate solution; 70 ml for every O-1 g of phosphorus pentoxide. Continue stirring until the phosphorus is precipitated. Digest at 50 to 60°C for an hour. Cool to room temperature and filter the precipitate on an ashless paper pulp pad, wash the precipitate with cold dilute nitric acid.

36.3.4 Transfer the funnel and the filter pad to the original beaker in which phosphorus was precipitated and wash down the precipitate by the dropwise addition of dilute ammonium hydroxide (1 : 1), finally washing the pad and funnel with hot water. Add 2 g of citric acid and pour the solution through the filter which might contain some yellow precipitate and catch the solution in another 400 ml beaker. Wash the beaker and paper several times with dilute ammonium hydroxide (1 : 20), then with hot water, and then with dilute hydrochloric acid (1 : 20), and finally for several times with dilute ammonium hydroxide (1 : 20). If the solution in the beaker is not clear, heat it to boiling and filter through the same paper. The volume at this juncture should be 150 ml. Neutralize the ammoniacal solution with concentrated hydrochloric acid and add one millilitre of concentrated hydrochloric acid in excess. Add

20 ml of magnesia mixture for every 0.1 g of phosphorus. Add concentrated ammonium hydroxide dropwise and continue stirring until the solution is ammoniacal and most of the phosphorus has been precipitated. Finally add 15 ml of concentrated ammonium hydroxide and allow the solution to stand overnight. Filter, wash the magnesium ammonium phosphate precipitate for several times with dilute ammonium hydroxide (1 : 20) until free from chloride.

36.3.5 Ignite the precipitate carefully in a platinum or silica crucible, at a low temperature until the carbon paper is burnt. Finally ignite to constant weight at 1000°C and weigh as Mg2P2O7.

36.3.6 Make a blank determination using the same procedure and same quantities of reagents, but without the sample.

36.4 Calculation

$$\text{Phosphorus, percent} = \frac{(A-B) \times 27.86}{C}$$

where

A = weight in g of the magnesium pyrophosphate precipitate

B = correction for the blank, and

C = weight in g of the sample represented by the aliquot used.

37. DETERMINATION OF CARBON (TOTAL) By THE DIRECT COMBUSTION GRAVIMETR METHOD

37.1 Determine the carbon content of the sample by following the procedure given under 6 with the following modifications. [REPRODUCE HERE THE PROCEDURE GIVEN IN 6 OF IS 1559:1961 WITH FOLLOWING CHANGES]

37.1.1 Use one to two grams of the sample.

37.1.2 Use a furnace temperature of 1100 to 1200°C.

38. DETERMINATION OE CARBON (TOTAL) BY THE DIRECICOMBUSTION VOLUMETRIC (ALTERNATE) METHOD

38.1 Determine the carbon content of the sample by following the procedure as given under 8.

41.2 Reagents- In addition to the reagents given under [REPRODUCE HERE THE REAGENTS GIVEN IN 5.3 OF IS 1559:1961]

5.3, the following reagents are required.

41.2.1 Sodium Peroxide - solid.

41.2.2 Dilute Sulphuric Acid- 1 : 200 (v/v).

41.2.3 Oxalic Acid Solution - 100 g/l. Dissolve 100 g of oxalic acid in water and dilute to one litre.

41.3 Procedure

41.3.1 Mix 0.5 g of the accurately weighed sample, for silicon in the 2 to 15 percent range, or 0.25 g of the sample for silicon in 15 to 25 percent range, in an iron crucible with 8 to 10 g of dry sodium peroxide as under 14.4.1.

41.3.2 Transfer the cold cake to a dry 500-ml casserole, dissolve in water, cover and add 80 ml of dilute sulphuric acid (1:1). Rinse the crucible thoroughly with hot water, adding the washings to the *casserole. Add 50 ml of oxalic acid solution and evaporate slowly to fumes.

41.3.3 Heat to dense white fumes and continue the fuming for 3 to 5 minutes, cool, add 200 ml of warm water, heat to dissolve sulphates. Filter through filter paper No. 40 into a 500-ml casserole and wash at least 20 times with hot dilute sulphuric acid (1 : 200). Further complete the estimation as described under 5.4.4 to 5.5. [REPRODUCE HERE THE PROCEDURE GIVEN IN 5.4.4 to 5.5 OF IS 1559:1961]

42. DETERMINATION OF CARBON (TOTAL) BY THE DIRECT COMBUSTION GRAVIMETRIC METHOD

42.1 Determine the carbon content of the sample by following the procedure as given under 33. REPRODUCE HERE THE PROCEDURE GIVEN IN 33 OF IS 1559:1961]

IS 1559 PART 10 :2022

METHODS OF ANALYSIS OF VANADIUM

43. DETERMINATION OF VANADIUM BY THE PERMANCANATE TITRATION METHOD

43.1 Outline of the Method - Vanadium in the sulphuric acid-nitric acid solution of the sample is oxidized to vanadic acid and then reduced by slight excess of ferrous solution, the excess of which is destroyed by ammonium persulphate, reduced vanadium is then titrated with standard permanganate solution.

*As the solution approaches the fuming point, bumping is likely to occur unless oxalic acid has been added which serves as an anti-bumping agent; some foaming occurs as the fuming point is reached but it does not harm.

43.2 Reagents

43.2.1 Sulphuric Acid-Nitric Acid Mixture - Mix two volumes of dilute sulphuric acid (1 : 3) with one volume of dilute nitric acid (1 : 1).

43.2.2 Hydrofluoric Acid - 40 percent.

43.2.3 Standard Potassium Permanganate Solution – 0.1 N.

43.2.4 Ferrous Ammonium Sulphate Solution – 0.1 N approximately.

43.2.5 Potassium Ferricyanide Indicator Solution - Dissolve 0.1 g of the reagent in 100 ml of water. Prepare fresh as needed.

43.2.6 Ammonium Persulphate Solution (95 percent pure) - 15 percent (w/v). Prepare fresh as needed.

43 Procedure

43.3.1 Transfer 0.25 to 0.5 g of the sample to a 600-ml beaker and add 80 ml of sulphuric acid-nitric acid mixture. If the silica content is high and the alloy fails to decompose completely, add a few millilitres of hydrofluoric acid substituting beaker with 200-ml platinum dish. After the reaction is over, evaporate the solution to dense white fumes. Cool, add 100 ml of water and heat until salts are dissolved.

43.3.2 Transfer the solution to a 800-ml beaker, dilute to 400 ml and to the cooled solution add standard potassium permanganate solution until a strong pink colour has developed that persists for 30 seconds. Cool the solution to 15°C and reduce vanadium by adding ferrous ammonium sulphate solution till the presence of ferrous iron is indicated by the ferricyanide spot test (fisted externally). Add 5 ml of ferrous ammonium sulphate solution in excess and stir the solution for at least one minute. Cool to 15°C and oxidize the excess ferrous iron with 8 to 10 ml of ammonium persulphate solution. Stir the solution vigorously for one minute. Titrate the solution with standard potassium permanganate solution until a faint pink colour appears and persists for 30 seconds.

43.4 Calculation

$$\text{Vanadium, percent} = \frac{A\ B \times 5.095}{C}$$

where

A = volume in ml of the standard potassium permanganate solution required for the titration,

B = normality of the standard potassium permanganate solution, and

C = weight in g of the sample taken.

44 DETERMINATION OF SILICON BY THE GRAVIMETRIC METHOD

44.1 Outline of the Method- The sample is dissolved in sulphuric acid-nitric acid mixture or in case of high-silicon alloy, fused with sodium peroxide and extracted with sulphuric acid. The solution is fumed to dehydrate silica and filtered. Silica is then hydrofluorized and estimated as usual.

44.2 Reagents - In addition to the reagents given under 5.3 the following reagents are required:

44.2.1 Sulphuric Acid-Nitric Acid Mixture - Slowly stir 160 ml of concentrated sulphuric acid (see 7.3.1) in 660 ml of water and add 180 ml of concentrated nitric acid

44.2.2 Sodium Peroxide - solid.

44.2.3 Potassium Bisulphate - solid.

44.3 Procedure

44.3.1 Dissolve 2 g of the accurately weighed sample of low-silicon alloy in 40 ml of sulphuric acid-nitric acid mixture in a platinum dish and evaporate to dense white fumes.

44.3.2 In case of high-silicon alloy fuse one gram of the accurately weighed sample with 8 g of sodium peroxide in 30-ml iron crucible as described under 14.4.1 REPRODUCE HERE THE PROCEDURE GIVEN IN 14.4.1 OF IS 1559:1961] . Extract the melt, with caution, with 80 ml of dilute sulphuric acid in a porcelain casserole. Evaporate the solution to dense white fumes.

44.3.3 Cool, add 125 ml of water and heat for a few minutes, stirring frequently, until all salts are dissolved. Immediately filter and wash the precipitate with hot dilute hydrochloric acid (1 : 20.) and hot water alternately to complete the removal of iron salts and finally wash with hot water until free from acid. Preserve the filtrate for the estimation of phosphorus and further complete the estimation as described under 5.33 to 5.5. [REPRODUCE HERE THE PROCEDURE GIVEN IN 5.33 to 5.5OF IS 1559:1961]

44.3.4 Fuse the residue after hydrofluorization in the platinum crucible with potassium bisulphate, extract the melt with Water and add it to the main filtrate reserved in 44.3.3 [REPRODUCE HERE THE PROCEDURE GIVEN IN 44.3.3 OF IS 1559:1961 for making the filtrate] for the estimation of phosphorus.

45. DETERMINATION OF AWMINIUM BY THE CUPFERRON-PHOSPHATE METHOD

45.1 Outline of the Method- From the sulphuric acid-nitric acid solution of the sample, vanadium and iron are separated by double precipitation with cupferron. Aluminium in the filtrate is precipitated, as hydroxide, dissolved in hydrochloric acid converted to phosphate in an alkaline medium, and weighed as aluminium phosphate.

45.2 Reagents

45.2.1 Dilute Sulphuric Acid- 1 : 2 (v/v).

45.2.2 Concentrated Nitric Acid- see 63.1.

45.2.3 Hydrofluoric Acid - 40 percent.

45.2.4 Potassium Permanganate Solution - 25 g/l.

45.2.5 Cupferron Solution -

45.2.6 Cupferron Wash Solution -

45.2.7 Concentrated Sulphuric Acid -

45.2.8 Ammonium Chloride - solid.

45.2.9 Bromocresol Purple Indicator Solution -

45.2.10 Dilute Ammonium Hydroxide - 1 : 1 (v/v).

45.2.11 Ammonium Chloride Solution - 20 g/l.

45.3.12 Dilute Hydrochloric Acid - 1 : 3 and I : 9 (v/v).

45.3.13 Diammonium Hydrogen Phosphate - solid.

45.2.14 Methyl Red Indicator - Dissolve 01 g of methyl red in 372 ml of 0.1 N sodium hydroxide and dilute to 250 ml with water. Filter, if necessary.

45.2.15 Ammonium Acetate Solution - 200 g/I.

45.3.16 Ammonium Nitrate Solution - 50 g/l.

45.3 Procedure

45.3.1 Decompose one gram of the sample with 60 ml of dilute sulphuric acid and 10 ml of concentrated nitric acid in a platinum dish. Add 2 to 3 ml of hydrofluoric acid and evaporate to dense white fumes. Cool a little, add water and heat to dissolve salts. Transfer to a 400-ml beaker and add potassium permanganate solution till a pink colour persists. Dilute to 100 ml and cool to 5 to 10°C. Add some ashless paper pulp and precipitate iron and vanadium by adding cupferron solution until an excess of the reagent is shown by the appearance of a white curdy precipitate instead of the brown one formed first. Stir vigorously for 2 to 3 minutes and filter through filter paper No. 41. Wash thoroughly with cupferron wash solution. Reserve the filtrate.

45.3.3 Return the precipitate to- the original beaker and add 10 ml of concentrated sulphuric acid and 50 ml of concentrated nitric acid and. evaporate to fumes. Add more concentrated nitric acid, if necessary, and repeat the evaporation to oxidize all organic matter. Cool, add 100 ml of water and digest until all salts are in solution. Cool to 5 to 10°C, add an excess of potassium permanganate and re-precipitate with cupferron solution. Filter and wash as in 45.3.1 [REPRODUCE HERE THE PROCEDURE GIVEN IN 45.3.1 OF IS 1559:1961 for filtering and washing] . Combine this filtrate with that reserved in 45.3.1.

45.3.3 To the combined filtrate, add 75 ml of concentrated nitric acid and evaporate to fumes. Add concentrated nitric acid again, if necessary, and evaporate to fumes to oxidize all organic matter. Cool, dilute with 100 ml water; add 10 g ammonium chloride and a few drops of bromocresol purple indicator solution. Add dilute ammonium hydroxide until the solution just turns purple. Boil the solution for one minute, allow to settle, filter and wash with warm ammonium chloride solution. Dissolve the precipitate in 50 ml of hot dilute hydrochloric acid (1 : 3) and repeat the precipitation with ammonia as before.' Dissolve the precipitate on the paper with 50 ml of hot dilute hydrochloric acid (1 : 3.) and wash the paper with hot water.

45.3.4 To the filtrate and washings, add 0.5 g of diammonium hydrogen phosphate, a little ashless paper pulp and two drops of methyl red indicator and make just ammoniacal. Restore the pink colour by adding dilute hydrochloric acid (1:9) drop by drop. Heat the solution to boiling and add 20 ml of ammonium acetate solution. Continue the boiling for 5 minutes, allow to settle, filter and wash with hot' ammonium nitrate solution till free from chlorides. Ignite in a porcelain crucible to constant weight at 950 to 1000°C. Weigh as aluminium phosphate.

45.3.5 Make a blank determination following the same procedure and using the same amounts of reagents but without the material.

45.4 Calculation

$$\text{Aluminium, percent} = \frac{(A - B) \times 22.1}{C}$$

where

A = weight in g of aluminium phosphate obtained,

B = correction for blank in g, and

C = weight in g of the sample taken.

46 DETERMINATION OF PHOSPHORUS BY THE ALKALI METRIC METHOD

46.1 Determine phosphorus content of the sample by following the procedure as given under 10 with the following modification.

46.1.1 Dilute the filtrate reserved under 44.3.4 [REPRODUCE HERE THE PROCEDURE GIVEN IN 44.3.4 OF IS 1559:1961 for making the filtrate] to about 200 ml, heat 'to boiling and add potassium permanganate solution until a pink colour persists during 5 minutes boiling. Further complete the estimation as under 10.3.3 to 10.4.

47. DETERMINATION OF SULPHUR BY THE GRAVIMETRIC METHOD

47.1 Outline of the Method -After removal of silica, from the nitric acid solution of the sample, followed by the recovery of sulphur from the silica residue, sulphur is precipitated from the reduced solution as barium sulphate, traces of barium vanadate are removed by reprecipitation and then barium sulphate is ignited and weighed.

47.2 Reagents - In addition to the reagents mentioned under 9.2 [REPRODUCE HERE THE reagents GIVEN IN 9.2 OF IS 1559:1961, the following reagents are required.

47.2.1 Dilute .Hydrochloric Acid - 3 : 97 (v/v).

47.2.2 Sodium Carbonate - anhydrous.

47.3 Procedure

47.3.1 Transfer 5 g of the sample to a large platinum dish and dissolve in 50 to 60 ml of concentrated nitric acid. Since the reaction is likely to be very rapid, the transfer of the sample is best done in small portions while keeping the dish cooled in ice water. In the case of high silicon alloys, add a few millilitres of hydrofluoric acid, warm if necessary, to complete the reaction. Add 30 ml of concentrated hydrochloric acid and one gram of sodium carbonate and evaporate to dryness on the steam-bath. Add 30 ml more of concentrated hydrochloric acid and again evaporate to dryness and bake for 30 minutes at 100 to 110°C. Moisten the residue with 30 ml concentrated hydrochloric acid and 25 ml of water, heat to dissolve salts and filter through filter paper No. 40 washing the paper and residue with dilute hydrochloric acid (3 : 97). Reserve the filtrate.

47.3.2 Ignite the paper and the residue in a platinum crucible, evaporate to dryness with a few millilitres of hydrofluoric acid and fuse with sodium carbonate. Extract the melt with water, filter and add the filtrate to that reserved in 47.3.1.

47.3.3 Evaporate the combined filtrate to syrupy consistency. Add 10 ml of concentrated hydrochloric acid, 25 ml of water and 4 to 5 g of zinc, and warm on a steam-bath until iron is reduced to the ferrous state. Filter off the undissolved zinc and wash with dilute hydrochloric acid. Dilute to 200 ml with dilute hydrochloric acid, warm to 50 to 60% and add 25 ml of barium chloride solution. Stir well and let stand at room temperature overnight.

47.3.4 Filter, with as little transfer of precipitate as possible, through filter paper No. 42, wash the paper two to three times with cold dilute hydrochloric acid and then with warm water. Ignite the paper and contents in a platinum crucible and dissolve the ignited residue in 5 ml of dilute hydrochloric acid and transfer the solution to the original beaker containing most of the barium sulphate. Digest the combined portions so as to dissolve any barium vanadate. Complete the estimation as described under 9.3.3 to 9.4. [REPRODUCE HERE THE PROCEDURE GIVEN IN 9.3.3 to 9.3.4 OF IS 1559:1961

48 DETERMINATION OF CARBON (TOTAL) BY THE DIRECT COMBUSTION GRAVIMETRIC METHOD

48.1 Determine the carbon content of the sample by following the procedure as given under 7 with the following modifications. [REPRODUCE HERE THE PROCEDURE GIVEN IN 7 OF IS 1559:1961 WITH THE FOLLOWING MODIFICATIONS]

48.1.1 Use one to two grams of the sample.

48.1.2 Use a furnace temperature of 1100 to 1200°C.

49. DETERMINATION OF CARBON (TOTAL) BY THE DIRECT COMBUSTION VOLUMETRIC (ALTERNATE) METHOD

49.1 Determine the carbon content of the sample by following the procedure as given under 8.

50. Quantitative determination of V, P, Mn, Si & Al in Ferro Vanadium by using ICP-OES technique (may be validated before incorporation)

50.1 This method shall be followed for determination of V, P, Mn, Si & Al in Ferro Vanadium for the following ranges of concentration

V% - 25 % to 80%

Mn% - 0.001% to 2.00%

P% - 0.01 % to 0.1%

Al% - 0.10% to 5.00%

Si% - 0.50% to 5.00%

50.2 Preparation of calibration solution

12 nos. of Synthetically Calibration Standard Solutions may be prepared with concentrations as below from NIST traceable 1000 ppm Standard Solution of individual element along with 1000 ppm Fe as base solution added and acidify with 5 ml HNO3 plus 2ml HF make up to 100ml volumetric flask by distilled water.

STD.No	Al (ppm)	Mn (ppm)	P (ppm)	V (ppm)	Si (ppm)	Fe (ppm)
Ferro alloy-1	**0.01**	**1**	**0.01**			**1000**
Ferro alloy-2	**0.05**	**5**	**0.05**			**1000**
Ferro alloy-3	**0.5**	**10**	**0.5**			**1000**
Ferro alloy-4	**1**	**20**	**1**			**1000**
Ferro alloy-5	**5**	**50**	**5**			**1000**
Ferro alloy-6	**10**	**100**	**10**			**1000**
Ferro alloy-7				**1**	**1**	**1000**
Ferro alloy-8				**5**	**5**	**1000**
Ferro alloy-9				**10**	**10**	**1000**
Ferro alloy-10				**20**	**20**	**1000**
Ferro alloy-11				**50**	**50**	**1000**
Ferro alloy-12				**100**	**100**	**1000**

50.3 Dissolution of Sample

50.3.1 0.5gm of sample shall be taken in Teflon beaker and 20ml of con. HNO3 added to digest it on hotplate for 15min. then add 2 to 5ml of HF keep it on hotplate till clear solution obtained and makeup it 250ml Plastic Volumetric Flask (If clear solution not obtained, filter it by using Whatman No.40 filter paper). This is the stock solution is used for analysis of Mn,Si,P &Al and 10 times of diluted solution from stock solution shall be used for analysis Vanadium (10ml from stock solution in 100ml v.f) then acidify with 5ml concentrated HNO3 + 2ml HF and makeup it up to the mark. Similarly, reagent blank solution shall also be prepared. A respective matrix matching CRM shall be used for validation of finding data.

50.4 **Calibration parameters for ICP-OES (Illustrative)**

Power(KW)	1.20
Plasma flow (L/min)	12.0
Auxiliary Flow	1.50
Nebulizer Flow	0.50
Viewing height	10.0
Replicate read time	5 sec.
Instrument stabilization delay	15 sec
Sample uptake delay	30 sec.
Pump rate (rpm)	15
Rinse time(s)	5
Replicate	2

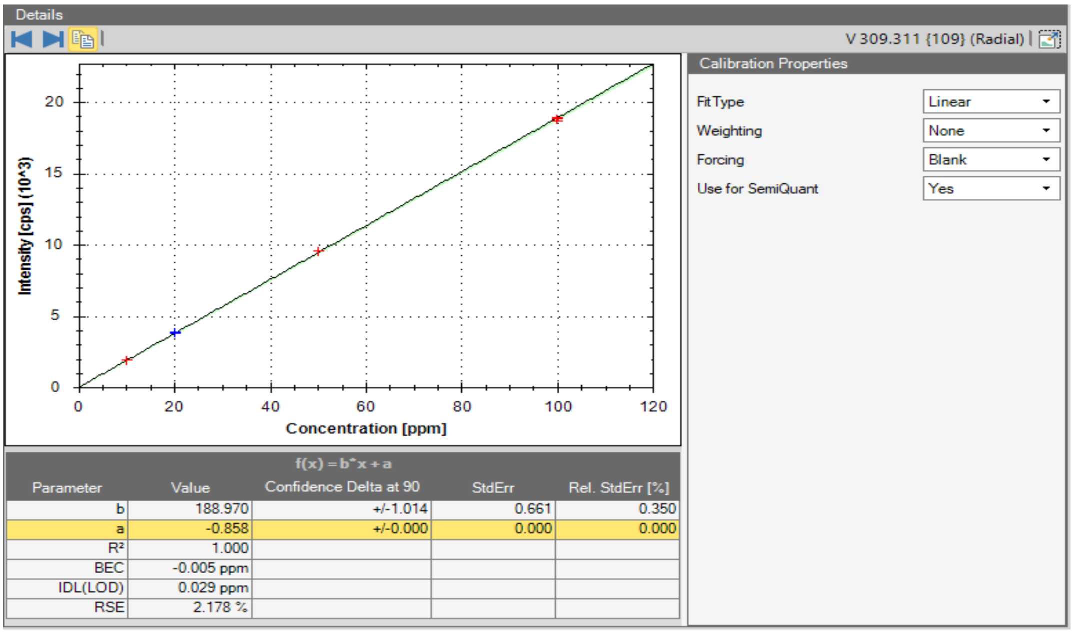
50.5 Wavelength selection for Ferro Vanadium:

Element	Wavelength (nm)
V	309.311 & 292.402 (Radial)
P	178.284 (Axial)
Mn	257.610,259.373(Axial)
Al	396.152(Axial)

50.6 Calibration profile shall be made with the help of software and Intensity v/s Concentration. Illustration is given below:

Illustrative Calibration graph

Vanadium at 309.311 nm:



Fit Type: Linear
Weighting: None
Forcing: Blank
Use for SemiQuant: Yes

f(x) = b*x + a

Parameter	Value	Confidence Delta at 90	StdErr	Rel. StdErr [%]
b	188.970	+/-1.014	0.661	0.350
a	-0.858	+/-0.000	0.000	0.000
R²	1.000			
BEC	-0.005 ppm			
IDL(LOD)	0.029 ppm			
RSE	2.178 %			

50.7 CRM results shall be analysed, and used as validation of the data (Note: For Vanadium ten times diluted solution are used). Illustrative results for EURONORM 577-1 CRM are given below

ERUONORM 577-1

CRM No	Sample wt (gm)	Volume (ml)	*V (ppm)	Mn (ppm)	P (ppm)	Al (ppm)	Si (ppm)
EURONORM 577-1A	0.5000	250	100.16	3.12	0.69	7.98	35.26
EURONORM 577-1B	0.5000	250	100.25	3.06	0.72	8.12	34.95
EURONORM	0.5004	250	101.02	2.98	0.62	8.22	35.69

577-1C							

50.8 Concentration shall be calculated as follows

$$\textbf{\% Conc. Of (V, Mn, P, Al \& Si)} = \frac{\textbf{(PPM*Final volume*Dilution factor) *100}}{\textbf{(Sample weight*}10^{6}\textbf{)}}$$

IS 1559 PART 11 :2022

METHODS OF ANALYSIS OF TUNGSTEN

50. DETERMINATION OF TUNGSTEN BY THE ACID DIGESTION-CINCHONINE (GRAVIMETRIC) METHOD

50.1 Outline of the Method -Tungsten is precipitated with cinchonine solution and the last traces recovered from the filtrate by a-benzoinoxime. The precipitate is filtered, washed arid ignited to constant weight. The impurities in tungsten are removed by fusion with sodium carbonate.

50.2 Reagents

50.2.1 Hydrofluoric Acid- 40 Percent.

50.2.2 Concentrated Nitric Acid - see 6.3.1.

50.2.3 Dilute Sulphuric Acid – 1:1 (v/v).

50.2.4 Dilute Ammonium Hydroxide – 1:1 (v/v).

50.2.5 Dilute Hydrochloric Acid - 1 : 1 and 1 : 99 (v/v).

50.2.6 Concentrated Hydrochloric Acid - see 5.3.3.

50.2.7 a-Benzoinoxime Solution - 30 g/l. Dissolve 3 g of a-benzoinoxime in 95 ml of acetone and 5 ml of cold water, filter, if necessary.

50.2.8 Cinchonine Solution - Dissolve 125 g cinchonine in one litre of dilute hydrochloric acid (1:1).

50.2.9 Cinchonine - a-Benzoinoxime Wash Solution - Dilute a mixture of 30 ml of cinchonine solution and 5 ml of a-benzoinoxime to one litre with water.

59.2.10 Sodium Carbonate - anhydrous.

50.2.11 Tartaric Acid - solid.

50.2.12 Hydrogen Sulphide - gas.

50.2.13 Concentrated Ammonium Hydroxide - sp gr 0.90.

50.3 Procedure

50.3.1 Transfer one gram of the sample ground to pass IS Sieve 15 to a covered platinum dish, add 5 ml of hydrofluoric acid and add concentrated nitric acid drop by drop while heating, until the sample is dissolved. Remove and rinse the cover, add 15 ml dilute sulphuric acid and heat cautiously on a sand bath to dense white fumes.

50.3.2 Allow to cool, transfer the residue to a beaker with water, finally wipe the dish with a piece of ashless filter paper and add the paper to the solution. Rinse the dish twice with a little warm dilute ammonium hydroxide, some water and then with a few millilitres of dilute hydrochloric acid and add to the main solution. Dilute the contents of the beaker to about 150 ml, add 10 ml of concentrated hydrochloric acid and boil for five minutes. Remove from the source of heat, dilute to 430 ml with water and add 10 ml of cinchonine solution. Keep overnight at room temperature and add 5 ml of a-benzoinoxime solution. Stir vigorously for several minutes and filter on an ashless paper pulp. Wash thoroughly with cinchonine - a-benzoinoxime wash solution and finally several times with cold dilute hydrochloric acid.

50.3.3 Ignite the residue gently in a Weighed platinum crucible. Add a few drops of concentrated nitric acid, dry on water bath and re-ignite at not more than 850°C to constant weight.

50.3.4 Fuse the residue with sodium carbonate and dissolve the fused mass in hot water containing a little alcohol, and filter. Wash the residue thoroughly with hot water. Repeat the fusion of the residue with sodium carbonate as before. Combine the filtrates of two fusions and preserve the combined filtrate. Ignite the paper and the residue, add one or two drops of concentrated sulphuric acid and one millilitre of hydrofluoric acid, evaporate to dryness and ignite again to constant weight.

50.3.5 Acidify the combined filtrate reserved under 503.4 with dilute sulphuric acid and add 8 ml of the acid in excess for each 100 ml of the solution. Add few grams of tartaric acid. Warm the solution and saturate it with hydrogen / sulphide gas. If molybdenum is indicated, filter the precipitate and dissolve in concentrated ammonium hydroxide. Determine the molybdenum content of the solution calorimetrically

50.3.6 Determine the amount of insoluble residue in the same weight of sodium carbonate as was used in the test (see 50.3.4)

50.4 Calculation

$$\text{Tungsten, percent} = \frac{[A- (B-C)] \times 79.3}{D} - F$$

where

A = weight in g of the impure tungstic oxide (WO3) obtained under 50.33,
B = weight in g of the insoluble residue obtained from sodium carbonate fusion (see 50.3.4),
C = weight in g of insoluble residue obtained from sodium carbonate used (see 50.3.6)
D = weight in g of the sample used, and
E = molybdenum oxide (M0 O2) percent as determined calorimetrically under 50.3.5.

51. DETERMINATION OF CARBON (TOTAL) BY THE DIRECT COMBUSTION GRAVMETRIC METHOD

51.1 The carbon content of the sample shall be determined by following the procedure as .given under 6 with the following modifications.

51.1.1 Use one to two grams of the sample.
51.1.2 Use a furnace temperature of 1100 to 1200°C.

52. DETERMINATION OF CARBON (TOTAL) BY THE DIRECT COMBUSTION VOLUMETRIC (ALTERNATE) METHOD

52.1 Determine the carbon content of the sample by following the procedure given under 8 with following modification.

52.1.1 Use O-5 g of the sample.

53. DETERMINATION OF SILICON BY THE GRAVIMETRIC METHOD

53.1 Outline of the Method- The sample is fused with sodium peroxide, extracted with water and silica dehydrated by means of sulphuric acid in presence of phosphoric acid which keeps tungsten in solution. Iron is dissolved by the addition of tartaric acid and the silica is filtered, ignited and hydrofluorized as usual.

53.2 Reagents- In addition to the reagents given under 5.3 the following reagents are required.

- **53.2.1** Sodium Peroxide - solid.
- **53.2.2** Phosphoric Acid- 85 percent.
- **53.2.3** Perchloric Acid- 70 percent.
- **53.2.4** Tartaric Acid Solutions - 5 and 8 percent (w/v).

53.3 Procedure

53.3.1 Fuse one gram of the sample with 10 g of dry sodium peroxide as under 14.4.1. [REPRODUCE HERE THE PROCEDURE GIVEN IN 14.4.1 OF IS 1559:1961

53.3.2 Cool and extract in a covered 600-ml tall-form beaker containing 50 ml of water. Remove the, crucible, wash thoroughly with water and acidify with 80 ml of dilute sulphuric acid. Transfer the contents of the beaker to a porcelain dish, add 5 ml of phosphoric acid and 10 ml of perchloric acid, evaporate to dense white fumes.

53.3.3 Allow to cool a little and add 200 ml of warm tartaric acid solution (8 percent). Heat at a temperature of 60 to 70°C while stirring occasionally until all ferric sulphate has dissolved. Filter and wash thoroughly with tartaric acid solution (5 percent). Complete the estimation as described under 5.4.4 to 5.5.

54. DETERMINATION OF MANGANESE BY THE BISMUTHATE METHOD

54.1 Outline of the Method -The sample is decomposed with nitric acid and hydrofluoric acid, evaporated to fumes with sulphuric acid. Tungstic acid is separated and the manganese recovered from the residue. The bivalent manganese in the solution is then oxidized to permanganic acid and estimated as usual.

54.2 Reagents - In addition to the reagents given under 19.2 [REPRODUCE HERE THE REAGENTS GIVEN IN 19.2 OF IS 1559:1961

the following reagents are required.

54.2.1 Concentrated Nitric Acid - see 6.3.1.
54.2.2 Hydrofluoric Acid - 40 percent.
54.2.3 Sodium Hydroxide Solution 10 percent (w/v).
54.2.4 Standard Ferrous Ammonium SuIphate Solution – 0.03 N. Dissolve 12 g of ferrous ammonium sulphate [$Fe(NH_4)_2(SO_4)_2, 6H_2O$] in cold dilute sulphuric acid (5:95) and make up to one litre with this acid. Mix well and keep in an amber-coloured glass-stoppered bottle.

54.2.5 Dilute Sulphuric Acid- 1 : 1 (v/v).

54.2.6 Standard Potassium Permanganate Solution: 0.03 N. Dissolve 0.958 g of potassium permanganate in water and dilute to one litre. Put the solution aside for two weeks in a dark place, filter without washing through a fritted glass crucible and store in a dark-coloured stoppered bottle. Standardize the permanganate solution against standard sodium oxalate solution (0.03 N). Analyse standard steel of known manganese content to check up the strength of the standard permanganate solution.

54.3 Procedure

54.3.1 Dissolve one gram of the sample in 15 ml of concentrated nitric acid and 5 ml of hydrofluoric acid in a platinum dish. Add 5 ml of concentrated sulphuric acid and evaporate to dense white fumes. Cool and add 50 ml of water. Heat to 80 to 90°C for 15 minutes, while stirring occasionally, and filter into a 300-ml Erlenmeyer flask. Preserve the filtrate. .

54.3.2 Place the filter and precipitate into a 250-ml beaker, add 50 ml of sodium hydroxide solution and boil for 5 minutes. Dilute to about 100 ml and filter through filter paper No. 541, washing six times with hot water. Reject the filtrate and washings. Dissolve the residue on the paper with hot dilute sulphuric acid and a few drops of sulphurous acid. Boil off the sulphurous acid, add the solution to the filtrate reserved under 54.3.1 and add 75 ml of concentrated nitric acid. Complete the estimation as described tinder 19.3.2 to 19.4 [REPRODUCE HERE THE PROCEDURE GIVEN IN 19.3.2 TO 19.4 OF IS 1559:1961 with the exception that potassium permanganatc and ferrous ammonium sulphate solutions used shall be 0.03 N.

55. DETERMINATION OF MANGANESE BY THE PERSULPHATE-ARSENITE (ALTERNATE) METHOD

55.1 Outline of the Method- After the separation of tungstic acid, manganese, in the solution of the sample, is oxidized with potassium persulphate in presence of silver nitrate and titrated rapidly with sodium arsenite solution.

55.2 Reagents - In addition to the reagents given under 54.2 [REPRODUCE HERE THE REAGENTS GIVEN IN 54.2 OF IS 1559:1961, the following reagents are required.

55.2.1 Silver Nitrate Solution - one percent (w/v).

55.2.2 Ammonium Persulphate Solution - 25 percent (w/v). Prepare fresh as needed.

55.2.3 Sodium Arsenite (Stock) Solution - To 15 g of arsenous oxide in a 500-ml flask, add 45 g of sodium carbonate and 150 ml of distilled water. Heat the flask and contents on the steam bath until the arsenous oxide is dissolved. Cool the solution, filter and make up to one litre with distilled water.

55.2.4 Standard Sodium Arsenite Solution - Mix 200 ml of the sodium arsenite (stock) solution with 2 500 ml of distilled water and standardize against potassium permanganate 0.01 N or a standard manganese alloy containing about one percent manganese, by dissolving 0.2 g of the latter in 30 ml of mixed acids (200 ml water, 400 ml of concentrated sulphuric acid and concentrated nitric acid).

55.3 Procedure

55.3.1 Dissolve one gram of the sample as described under 54.3.1 and 53.3.2. Add 100 ml of hot water, 10 ml of silver nitrate solution, 10 ml of ammonium persulphate solution and 5 ml of phosphoric acid. Heat to boiling and boil briskly for one to two minutes. Add 75 ml of water to the solution, cool to about 30°C and titrate rapidly with standard sodium arsenite solution to a clear yellow end point that remains unchanged on further addition of the standard arsenite solution. If the solution is not titrated rapidly, part of the manganese may be reoxidized by the ammonium persulphate during the titration and thus yield high results.

45.4 Calculation

$$\text{Manganese, percent} = \frac{AB}{C} \times 100$$

where

A = volume in ml of the standard sodium arsenite solution required to titrate the sample,
B = manganese equivalent of the sodium arsenite solution in g per ml as determined, and
C = weight in g of the sample taken.

56. DETERMINATION OF TIN BY THE IODIMETRIC METHOD

56.1 Outline of the Method - The solution of the sample is made in nitric acid and hydrofluoric acid. Copper, tin, antimony, etc, are precipitated as sulphides with hydrogen sulphide treatment in acid medium. Tin, alongwith arsenic and antimony, is separated, dissolved in hydrochloric acid and potassium chlorate and antimony precipitated by passing hydrogen sulphidc through the solution in presence of oxalic acid. Tin in the solution is then reduced to stannous chloride and titrated against potassium iqdate in presence of sodium bicarbonate.

56.2 Apparatus - The apparatus for the reduction of tin as shown in Fig. 5 shall be used.

56.3 Reagents

56.3.1 Concentrated Nitric Acid -
56.3.2 HydropUoric Acid - 40 percent.
56.3.3 Concentrated Srdphuric Acid - see 73.1.
56.3.4 Dilute Ammonium Hydroxide - 1:1 (v/v).
56.3.5 Dilute Sulphuric Acid - 1:1 (v/v).
56.3.6 Tartaric Acid - solid.
56.3.7 Concentrated Ammonium Hydroxide – sp gr 0.90.
56.3.8 Hydrogen Sulphide – gas
56.3.9 Tartaric Acid Wash Solution - Dissolve 10 g of tartaric acid in one litre of dilute sulphuric acid (1:99) and saturate with hydrogen sulphide gas.

56.3.10 Potassium Hydroxide - Potassium Sulphide Solution - Saturate 250 ml of potassium hydroxide (100 g/l) with hydrogen sulphide gas and then add 750 ml of potassium hydroxide (100 g/l).
56.3.11 Sodium Peroxide - solid.
56.3.12 Potassium Hydroxide-Potassium Sulphide Wash Solution - Dilute 100 ml of the above solution to one litre.

56.3.13 Concentrated. Hydrochloric Acid -
56.3.14 Hydrogen Sulphide Wash Solution - Saturate dilute hydrochloric acid (1:99) with hydrogen sulphide gas.

56.3.15 Potassium Chlorate - solid.
56.3.16 Oxalic Acid- solid.
56.3.17 Hydrogen SuIphide - Oxalic Acid Wash Solution - Saturate dilute sulphuric acid (1:99) with hydrogen sulphide and dissolve in the solution a few crystals of oxalic acid for each 100 ml.

56.3.18 Ferric Sulphate Solution - 10 g/l.
56.3.19 Dilute Hydrochloric Acid - 1 : 1 (v/v).
56.3.20 Test Lead

56.3.21 Sodium Bicarbonate Solution - saturated.

56.3.22 Starch Solution - Make a suspension of one gram of soluble starch in about 10 ml of water and add it carefully to 100 ml of boiling water. Boil for two or three minutes and cool. Prepare fresh as needed.

56.3.23 Potassium Iodide - solid

56.3.24 Standard potassium Iodate Solution - 0.03 N. Di0073 solve 1.20 g of recrystallized potassium iodate in 200 ml of water containing one gram of sodium hydroxide and add 19 g of potassium iodide. When solution is complete dilute to one litre in a volumetric flask. To standardize, dissolve 002 g of tin in hydrochloric acid, reduce the tin with test lead and titrate with potassium iodate solution as described under 56.4.5.

56.4 Procedure

56.4.1 Transfer 5 g of the sample to a platinum dish provided with a cover and add 50 ml of concentrated nitric acid. Add hydrofluoric acid a little at a time, with occasional heating, until the alloy is dissolved. Evaporate to approximately 25 ml, add 35 ml of concentrated sulphuric acid and continue the evaporation to dense white fumes. Cool and transfer to a 600-ml beaker rinsing the dish successively with dilute ammonium hydroxide and hot dilute sulphuric acid and finally with water. Dilute to about 400 ml, add 20 g of tartaric acid and an excess of concentrated ammonium hydroxide. Heat just short of boiling for several minutes, acidify with concentrated sulphuric acid, adding an excess of 2 ml for every 100 ml of solution and pass a brisk stream of hydrogen sulphide gas at least 30 minutes. Filter and wash with tartaric acid wash solution.

54.4.2 Return the paper and sulphides to the beaker in which the precipitation was made and add 50 ml of potassium hydroxide potassium sulphide solution and one gram of sodium peroxide. Gradually heat to boiling with occasional stirring, dilute with an equal volume of water, filter into a 400-ml beaker and wash with potassium hydroxide-potassium sulphide wash solution. Discard the residue.

56.4.3 Add concentrated hydrochloric acid to the filtrate until the solution is acidic and then one millilitre in excess for every 100 ml of solution. Filter the sulphides and wash with hydrogen sulphide wash solution. Transfer the paper and precipitate to a 400-ml beaker, treat with 10 ml of concentrated hydrochloric acid and add potassium chlorate, a few crystals at a time, while warming the solution to 40°C. Dilute to 200 ml and boil gently to expel chlorine. Add 5 g of oxalic acid, heat to 70°C and pass in a rapid stream of hydrogen sulphide gas for 20 to 30 minutes. Fiiter and wash thoroughly with hydrogen sulphide-oxalic acid wash solution. Preserve the filter paper and the precipitate for the determination of antimony.

56.4.4 Add 5 ml of concentrated sulphuric acid to the filtrate and evaporate to dense white fumes. Cool somewhat and dilute, with 100 ml of water. Add 50 ml of ferric sulphate solution and heat to boiling. Add dilute ammonium hydroxide till the solution is alkaline, then add 5 ml in excess. Let the precipitate settle, filter and wash with hot water.

56.4.5 Dissolve the precipitate in 80 ml of hot dilute hydrochloric (1:1) and wash the filter with hot water collecting the solution in a 500-ml Erlenmeyer flask. Add one to two grams of test lead and close the flask with a one-holed rubber stopper carrying a bent delivery tube as shown in Fig. 5. Boil gently on a hot-plate for 20 minutes. At the end of this period immerse the delivery tube in a small beaker containing saturated sodium bicarbonate solution. Remove the flask from the hot plate and keeping the delivery tube immersed in sodium bicarbonates, allow to cool to room temperature. Remove the stopper, add 5 ml of starch solution, 2 to 3 g of potassium iodide and titrate with standard potassium iodate solution to a permanent blue colour.

56.4.6 Make a blank determination following the same procedure and using the same amounts of reagents, but without the material.

56.5 Calculation

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

where

A = volume in ml of the standard potassium iodate solution required for the sample,
B = volume in ml of the standard potassium iodate solution required for the blank,
C = tin equivalent of potassium iodate solution in g/ml, and
D = weight in g of the sample taken.

57. DETERMINATION OF ANTIMONY BY THE GRAVIMETRIC

57.1 Outline of the Method - The precipitate reserved under 56.43 is dissolved by means of hydrochloric acid and bromine. Iron and antimony are co-precipitated, dissolved in hydrochloric acid in presence of tartaric acid. Iron is reduced by ammonium bisulphite and antimony precipitated from the acid solution as sulphide. It is ignited to constant weight and weighed as Sb2O4.

57.2 Reagents

57.2.1 Dilute Hydrochloric Acid- 1 : 3 and 1 : 9 (v/v).
57.2.2 Bromine – liquid
57.2.3 Ferrous Sulphate - solid.
57.2.4 Potassium Chloride - solid.
57.2.5 Concentrated Hydrochloric Acid - see 5.3.3.
57.2.6 Concentrated Nitric Acid - see 6.3.1.
57.2.7 Dilute Ammonium Hydroxide - 1 : 1 (v/v).
57.2.8 Tartaric Acid- solid.
57.2.9 Ammonium Bisulphite Solution – 200 g/l.
57.2.10 Hydrogen Sulphide - gas.
57.2.11 Hydrogen Sulphide Wash Solution - Saturate dilute hydrochloric acid (1:99) with hydrogen sulphide.
57.2.12 Ethyl Alcohol
57.2.13 Ether
57.2.14 Carbon Disulphide

57.3 Procedure

57.3.1 Dissolve the precipitate reserved in accordance with 56.4.3 in dilute hydrochloric acid (1:9) containing few drops of bromine, keeping the volume down to 25 ml. Evaporate the solution to about 5 ml on a steam bath, add one gram of ferrous sulphate, 0.5 g of potassium chloride and 40 ml of concentrated hydrochloric acid. Evaporate the solution again on a steam bath to 5 ml, dilute with 10 ml water; add one millilitre of concentrated nitric acid and heat until the iron is oxidized. Dilute to 100 ml, heat to boiling, add dilute ammonium hydroxide in slight excess, let the precipitate settle, filter off and wash with warm water.

57.3.2 Dissolve the precipitate in 10 to 15 ml of hot dilute hydrochloric acid (1:3) containing 0.1 g of tartaric acid. Dilute to 100 ml, heat and add ammonium bisulphite solution drop by drop to reduce the iron. Boil to expel sulphur dioxide, cool and pass a rapid stream of hydrogen sulphide gas for 15 to 30 minutes. Filter through a weighed Gooch crucible and wash successively with hydrogen sulphide wash solution, alcohol, ether and carbon disulphide. Heat the crucible and precipitate gently, adding one drop of concentrated nitric acid from time to time to oxidize the antimony sulphide. Finally heat at about 600°C to constant weight and weigh as Sb2O4.

57.4 Calculation

$$\text{Antimony, percent} = \frac{A \times 79.2}{B}$$

where

A = weight in g of the antimony oxide, and
B = weight in g of the sample taken.

58. DETERMINATION OF ARSENIC BY THE HYPOPHOSPHITE (IODIMETRIC) METHOD

58.1 Outline of the Method - The sample is fused with sodium peroxide, the melt extracted with water and tungsten kept in solution by phosphoric acid. Arsenic is reduced by sodium hypophosphite to metallic arsenic, in acid medium, and oxidized by a measured excess of standard iodine solution to pentavalent arsenic. The excess iodine is back-titrated with standard arsenious oxide solution.

58.2 Reagents

58.2.1 Sodium Peroxide – solid
58.2.2 Sodium Carbonate - anhydrous.
58.2.3 Phosphoric Acid -85 percent.
58.2.4 Concentrated Hodrochloric Acid - see 5.33.
58.2.5 Sodium Hypophosphite - solid.
58.2.6 Hydrofluoric Acid - 40 percent.
58.2.7 Dilute Hydrochloric Acid - 1 : 3 (v/v).
58.2.8 Ammonium Chloride Solution - 5 percent.

58.2.9 Standard Iodine Solution - 0.01 N. Dissolve 0.025 4 g of iodine and 3 g of potassium iodide in 20 ml water and dilute to 200 ml in a volumetric flask.

58.2.10 Standard Arsenious Oxide Solution - 0.01 N. Dissolve 0.099 of arsenious oxide a few millilitres of sodium hydroxide (20 percent) and dilute to 100 ml with water. Pass a brisk current of carbon dioxide for several minutes and then dilute to 200 ml.

58.2.11 Starch Solution - see 56.3.22.
58.2.12 Sodium Bicarbonate - solid, carbonate free.

58.3 Procedure

58.3.1 Transfer 5g of an accurately weighed sample, log of dry sodium peroxide and 5 g of sodium carbonate to an iron crucible, mix thoroughly with a glass rod and fuse carefully over a Bunsen flame. Just before completion of the fusion, increase the temperature to bright redness for one minute.

58.3.2 Extract the melt with a mixture of 100 ml of water and 40 ml of phosphoric acid in a flask, and rinse the crucible thoroughly pith water. Boil it down to about 50 ml. Cool and add 80 ml of concentrated hydrochloric acid and 40 ml of water. Add 2 g of sodium hypophosphite, warm to brisk effervescence, avoiding boiling, and add further 2 g of sodium hypophosphite until no further effervescence occurs.

Add 10 drops of hydrofluoric acid and 12 g of sodium hypophosphite and boil under reflux for 15 minutes.

58.3.3 Cool, filter off the precipitated arsenic and wash the residue first with 100 ml of dilute hydrochloric acid containing 3 g of sodium hypophosphite, then about seven times with ammonium chloride solution. Discard the filtrate, transfer the residue and filter to an 800-ml tall-form beaker, rinsing with about 50 ml of water.

58.3.4 Add a measured excess of the standard iodine solution, stir, allow to stand for five minutes, then dilute to 250 ml and titrate with arsenious oxide solution to pronounced lightening of iodine colour. Treat with a few millilitres of starch solution and discharge the colouration by adding about 3 ml more of the standard arsenious oxide solution and about 2 g of sodium bicarbonate. With vigorous shaking continuously, back-titrate with standard iodine solution.

58.3.5 Make a blank determination using the same amounts of all reagents, but without the material.

57.4 Calculation

$$\text{Arsenic, percent} = \frac{A - (B + C) \times 0.00015}{D} \times 100$$

57.4 Calculation

$$\text{Antimony, percent} = \frac{A \times 79.2}{B}$$

where

A = volume in ml of 001 N iodine solution used in the test titration,
B = volume in ml of 0.01 N iodine solution equivalent to the standard arsenious oxide solution used,
C = volume in ml of 0.01 N iodine solution consumed by the blank titration, and
D = weight in g of the sample taken.

59. DETERMINATION OF PHOSPHORUS BY THE ALKALIMETRIC METHOD

59.1 Determine phosphorus content of the sample by following the procedure as given under 10.3 with the following modification.

59.1.1 Dissolve 2 g of the sample in 15 ml of concentrated nitric acid and 5 ml of hydrofluoric acid in a platinum dish, and when decomposition is complete, add 5 ml of perchloric acid and 20 ml of concentrated sulphuric acid. Evaporate to dense white fumes. Cool, dilute with water, boil and filter. Wash the precipitate with hot water, collect filtrate and washings. Further complete the estimation as under 10.3.2 to 10.4.

60. DETERMINATION OF SULPHUR BY THE GRAVIMETRIC METHOD

60.1 Outline of the Method - The sample is dissolved in nitric acid, hydrofluoric acid and the tungsten separated as tungstic acid. The residual tungstic acid from the filtrate is removed by a-benzoinoxime solution in presence of cinchonine and sulphur estimated as usual.

60.2 Reagents - In addition to the reagents given under 9.2, the following reagents are required.
60.2.1 Sodium Carbonate - anhydrous.

60.2.2 Perchloric Acid - 70 percent.
60.2.3 Cinchonine Solution - Wash the cinchonine with water to remove any sulphate and then dissolve 125 g in one litre of dilute hydrochloric acid (1:1).
60.2.4 a-Benzoinoxime Solution - see 35.2.2.
60.2.5 a-Benzoinoxime Wash Solution - see 35.2.3.

60.3 Procedure

60.3.1 Transfer 5 g of the sample to a platinum dish and add 100 ml of concentrated nitric acid followed by hydrofluoric acid, a few drops at a time, and heating till the alloy has dissolved completely. Add one gram of sodium carbonate and 30 ml of perchloric acid, evaporate carefully to a syrupy condition. Cool a little, add 100 ml of boiling water and 5 ml of concentrated hydrochloric acid, digest for 30 minutes at 60 to 70° C and filter. Wash the precipitate of tungstic acid with hot dilute hydrochloric acid, Reject the precipitate.

60.3.2 Dilute the filtrate to 250 to 300 ml with hot water, add 5 ml of cinchonine solution and boil for three to five minutes. Cool to 15 to 20° C, add some ashless paper pulp and 5 to 10 ml of a-benzoinoxime solution, stir well for several minutes and filter. Wash the paper and precipitate 10 to 12 times with cold a-benzoinoxime wash solution. Reject the residue. Further complete the estimation as described under 9.3.2 to.9.4.