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धात्विक मैंगनीज के रासायनिक  
विश्लेषण — पद्धतियाँ  
( पहला पुनरीक्षण )

Chemical Analysis of Metallic  
Manganese — Methods  
( First Revision )

ICS 77.120.99

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## FOREWORD

This Indian Standard (First Revision) was adopted by the Bureau of Indian Standards, after the draft finalized by the Methods of Chemical Analysis of Metals Sectional Committee had been approved by the Metallurgical Engineering Division Council.

This standard was first published in 1967 and it recommends standard methods for the analysis of metallic manganese, which is used in ferrous and non-ferrous industries. In order to determine correctly the chemical composition of metallic manganese, need was felt to prescribe standard methods of analysis, so that these may primarily serve as referee methods and may also be used by laboratories for routine analysis. Due consideration has been given in the preparation of this standard to the facilities available in the country for such analysis.

In the formulation of this standard due weightage has been given to international co-ordination among the standards and the practices prevailing in different countries, in addition to relating it to those followed in this country.

In this revision has been brought out to bring the standard in the latest style and format of the Indian Standards.

The composition of the Committee responsible for the formulation of this standard is given in Annex A.

In reporting the results 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 : 2022 'Rules for rounding off numerical values (*second revision*)'.

*Indian Standard*

# CHEMICAL ANALYSIS OF METALLIC MANGANESE — METHODS

( *First Revision* )

## 1 SCOPE

This standard prescribes methods for chemical analysis of the two grades of metallic manganese, that is, Grade M Mn 95 and Grade M Mn 95 LC of IS 2021.

## 2 REFERENCES

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

<i>IS No.</i>	<i>Title</i>
IS 264 : 2005	Nitric acid — Specification ( <i>third revision</i> )
IS 265 : 2021	Hydrochloric acid — Specification ( <i>fifth revision</i> )
IS 266 : 1993	Sulphuric acid — Specification ( <i>third revision</i> )
IS 1070 : 2023	Reagent grade water — Specification ( <i>fourth revision</i> )
IS 1472 : 1977	Methods of sampling ferro- alloys for determination of chemical composition ( <i>first revision</i> )
IS 2021 : 1993	Manganese metal — Specification ( <i>second revision</i> )

## 3 SAMPLING

Samples shall be drawn and prepared in accordance with the procedure laid down for the purpose of chemical analysis in IS 1472.

## 4 QUALITY OF REAGENTS

Unless otherwise specified, pure chemicals and distilled water (*see* IS 1070) shall be employed in the tests.

NOTE — 'Pure chemicals' shall mean chemicals that do not contain impurities which affect the test results.

## 5 GENERAL

### 5.1 Use of Filter Papers

In some of the methods prescribed in this standard relative numbers of Whatman filter papers, which are commonly used, have been specified. However, any other suitable brand of filter papers of corresponding porosity may also be used.

## 6 DETERMINATION OF MANGANESE BY THE BISMUTHATE (VOLUMETRIC) METHOD

### 6.1 Outline of the Method

Manganese in the solution of the sample is oxidized to permanganic acid by means of sodium bismuthate in nitric acid medium, and the permanganate thus formed is reduced by a measured volume of standard ferrous ammonium sulphate solution, excess of which is titrated with standard potassium permanganate solution.

### 6.2 Reagents

**6.2.1 Dilute Nitric Acid** — 1 : 3, 3 : 97 and 5 : 95 (v/v)

#### 6.2.2 Sodium Bismuthate

The reagent should contain not less than 70 percent to 78 percent of active oxygen, as calculated for NaBiO<sub>3</sub>, or more than 0.002 percent of chlorine ions, or more than 0.001 percent of manganese.

**6.2.3 Standard Ferrous Ammonium Sulphate Solution** (0.1 N)

Dissolve 39.2 g of ferrous ammonium sulphate crystals [Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>.6H<sub>2</sub>O] in cold dilute sulphuric acid (5 : 95) and make up to 1 litre with this acid in a volumetric flask. Standardize against standard potassium permanganate solution (*see* 6.2.5).

**6.2.4 Phosphoric Acid** — 85 percent

**6.2.5 Standard Potassium Permanganate Solution** (0.1 N)

Dissolve 3.2 g of potassium permanganate in 1 litre

of water. Let it 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 materials. Store in a dark-coloured glass stoppered bottle. Standardize against analar sodium oxalate by weighing 0.134 g of the salt and dissolving in 250 ml of dilute sulphuric acid (5 : 95) and titrate against the permanganate at 55 °C to 60 °C to a faint pink end-point. Adjust the strength of the permanganate solution such that 0.134 g of sodium oxalate requires exactly 20 ml of the permanganate solution.

### 6.3 Procedure

**6.3.1** Transfer 1 g of the accurately weighed sample to a 400 ml beaker, and digest it with 60 ml of dilute nitric acid (1 : 3). Cover the beaker with watch-glass and heat the solution gently on a hot-plate, and when the sample is dissolved, boil it to remove all the nitrous fumes. Allow to cool and settle. If there is any residue, filter it through a filter paper and wash with dilute nitric acid (3 : 97). Transfer the solution to a 500 ml measuring flask and make up the volume with dilute nitric acid (1 : 3).

**6.3.2** Transfer an aliquot from the solution of the sample so that it contains 0.05 g to 0.10 g of manganese. Dilute with water to 100 ml. In order to destroy the organic matter and to oxidize other reducers, add to the solution, which has been heated to boiling, 1 g of sodium bismuthate in small portions. If, during boiling, the pink colour of manganic acid disappears or the residue of manganese dioxide dissolves, it is necessary to add a further quantity of sodium bismuthate. The formation of permanent precipitate of manganese dioxide indicates complete oxidation of organic and other matter. Whilst still boiling add dropwise standard ferrous ammonium sulphate solution until complete solution of the precipitate of manganese dioxide is obtained.

**6.3.3** Cool the solution to 10 °C to 15 °C. Add 2.6 g of sodium bismuthate for each 0.1 g of manganese to the cooled solution and stir vigorously for two min. Add 50 ml of cold dilute nitric acid (1 : 3) and filter immediately through a funnel packed with ignited asbestos and glass wool. The filtrate should be colourless. Wash the filter and the residue with cold dilute freshly boiled nitric acid (5 : 95) until washings are entirely colourless.

**6.3.4** Add to the filtrate a measured excess of standard ferrous ammonium sulphate solution, and 5 ml of phosphoric acid. Stir and titrate the excess

with standard potassium permanganate solution to the appearance of faint pink colour.

**6.3.5** Carry out a blank determination through all stages of the procedure using the same amount of standard ferrous ammonium sulphate solution as is added under **6.3.4** and titrate with standard potassium permanganate solution.

#### NOTES

**1** The asbestos used in titration should not contain organic admixture or other matter that may be titrated by the solution of potassium permanganate.

**2** To clean the asbestos, split it up into fibers, treat while heating with concentrated hydrochloric acid, and wash thoroughly with water. Then treat it while heating with dilute nitric acid (1 : 3) and wash with water to remove chlorine ions. Dry the washed asbestos, and heat to a temperature of 500 °C to 600 °C.

### 6.4 Calculation

$$\text{Manganese, percent} = \frac{(A - B) C \times 1.10}{D}$$

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 solution;

*C* = normality of the standard permanganate solution; and

*D* = mass, in g, of the sample represented by the aliquot taken.

## 7 DETERMINATION OF SILICON BY THE NITRIC-SULPHURIC ACID (GRAVIMETRIC) METHOD

### 7.1 Outline of the Method

The sample is taken to fumes with nitric-sulphuric acid mixture and soluble salts dissolved in hydrochloric acid. The solution is filtered and the silica ignited and determined by the loss in mass after volatilization with hydrofluoric acid in the presence of sulphuric acid.

### 7.2 Reagents

#### 7.2.1 Nitric-Sulphuric Acid Mixture

Slowly stir 160 ml of concentrated sulphuric acid into 660 ml of water, and add 180 ml of concentrated nitric acid.

**7.2.2 Concentrated Hydrochloric Acid** — specific gravity 1.16 (conforming to IS 265)

**7.2.3 Dilute Hydrochloric Acid** — 5 : 95 (v/v)

**7.2.4 Dilute Sulphuric Acid** — 1 : 1 (v/v)

**7.2.5 Hydrofluoric Acid** — 40 percent

### 7.3 Procedure

**7.3.1** Dissolve 1 g of the accurately weighed sample in 50 ml of nitric sulphuric acid mixture in 250 ml porcelain vessel and evaporate gently to dense white fumes.

**7.3.2** After the solution has cooled somewhat, add 125 ml of water and 5 ml of concentrated hydrochloric acid. Heat, while stirring frequently until all salts are dissolved and immediately filter through No. 40 filter paper. Wash the precipitate with hot dilute hydrochloric acid and hot water alternatively to complete the removal of soluble salts and finally with hot water until free from acid.

**7.3.3** Transfer the paper and the precipitate to a platinum crucible. Char the paper carefully, constant mass cover the crucible and ignite at 1 050 °C to cool in a desiccator and weigh.

**7.3.4** Moisten the ignited silica with a few drops of dilute sulphuric acid, add 5 ml of hydrofluoric acid, evaporate to dryness and continue heating until all the sulphuric acid fumes are completely eliminated. Complete the ignition in the muffle at 1 050 °C. The loss in mass represents silica.

### 7.4 Calculation

$$\text{Silicon, percent} = \frac{A \times 46.72}{B}$$

where

*A* = mass, in g, of silica obtained; and

*B* = mass, in g, of the sample taken.

## 8 DETERMINATION OF SULPHUR BY THE GRAVIMETRIC METHOD

### 8.1 Outline of the Method

After repeated evaporation with nitric acid and hydrochloric acid, the dry mass is taken up with hydrochloric acid and iron reduced with zinc. From the filtrate, sulphur is precipitated in acid medium as barium sulphate which is then ignited and weighed.

### 8.2 Reagents

**8.2.1 Concentrated Nitric Acid** — specific gravity 1.42 (conforming to IS 264)

**8.2.2 Sodium Chloride** — solid

**8.2.3 Concentrated Hydrochloric Acid** — as in 7.2.2

**8.2.4 Zinc** — granulated and sulphur-free

**8.2.5 Dilute Hydrochloric Acid** — 1 : 99 (v/v)

**8.2.6 Barium Chloride Solution** — 10 percent (w/v)

**8.2.7 Hydrochloric Acid Wash Solution**

Dilute 5 ml of concentrated hydrochloric acid with water to 1 000 ml and add 1 g of barium chloride.

### 8.3 Procedure

**8.3.1** Dissolve 5 g of the accurately weighed sample in 75 ml of concentrated nitric acid. When solution is complete, add 0.5 g of sodium chloride and carefully evaporate to dryness in a sulphur-free atmosphere. Bake for 15 min to 20 min on a hot-plate. Cool, add 30 ml of concentrated hydrochloric acid and warm gently until salts are dissolved and evaporate to syrupy consistency.

**8.3.2** Add 10 ml of concentrated hydrochloric acid, 25 ml of water, and 5 g of zinc, and warm on a steam-bath until the iron is reduced to the ferrous state and the evolution of hydrogen has nearly ceased. Filter and wash with 75 ml of dilute hydrochloric acid.

**8.3.3** Warm the filtrate to 60 °C to 70 °C and add dropwise 20 ml of barium chloride solution. Stir vigorously and let stand for 18 h to 24 h. Filter and wash with cold hydrochloric acid wash solution, then with hot water until free of chlorides. Dry and ignite the precipitate in a weighed platinum or porcelain crucible at 800 °C and weigh as barium sulphate.

NOTE — The solution should preferably contain not more than 2 percent by volume of concentrated hydrochloric acid at the time of precipitation with barium chloride.

**8.3.4** Carry out the blank determination following the same procedure and using the same amounts of all the reagents but without the sample.

### 8.4 Calculation

$$\text{Sulphur, percent} = \frac{(A - B)}{C} \times 13.74$$

where

*A* = mass, in g, of barium sulphate obtained in the test;

*B* = mass, in g, of the barium sulphate obtained in the blank; and

*C* = mass, in g of the sample taken.

## 9 DETERMINATION OF PHOSPHORUS BY THE ALKALIMETRIC METHOD

### 9.1 Outline of the Method

The sample is dissolved in nitric acid and phosphorus is precipitated as ammonium phosphomolybdate, which, after washing is dissolved in known excess of standard alkali. The unreacted alkali is back titrated with standard sulphuric acid.

### 9.2 Reagents

**9.2.1 Concentrated Nitric Acid** — as in 8.2.1

**9.2.2 Potassium Permanganate Solution** — 2.5 g/l

**9.2.3 Sulphurous Acid Solution**

Saturate water with sulphur dioxide. Prepare fresh as needed.

**9.2.4 Ammonium Nitrate** — solid

**9.2.5 Ammonium Molybdate Solution**

Add Solution A (see 9.2.5.1) slowly and with constant stirring to Solution B (see 9.2.5.2) kept cool in a cold water bath. Add 10 ml of ammonium phosphate solution (1 g/l) and keep the solution for at least 24 h. Filter the solution before use.

**9.2.5.1 Solution A**

Dissolve 100 g of molybdic acid (85 percent  $\text{MoO}_3$ ) in a mixture of 150 ml of concentrated ammonium hydroxide and 270 ml of water. Cool the solution.

**9.2.5.2 Solution B**

Add 490 ml of concentrated nitric acid to 1 150 ml of water and cool.

**9.2.6 Dilute Nitric Acid** — 2 : 98 (v/v)

**9.2.7 Potassium Nitrate Wash Solution** — 1 percent (w/v)

**9.2.8 Sodium Hydroxide Solution** — 0.1 N approximately

**9.2.9 Phenolphthalein Indicator Solution**

Dissolve 0.5 g of the reagent in 100 ml of alcohol (60 percent).

**9.2.10 Standard Sulphuric Acid** — 0.1 N

Dilute 2.5 to 3 ml of concentrated sulphuric acid to 1 litre and standardize against sodium carbonate.

### 9.3 Procedure

**9.3.1** Transfer about 1 g of the accurately weighed sample to a 300 ml Erlenmeyer flask. Dissolve the sample in 15 ml of concentrated nitric acid, heat gently to expel brown fumes and add 100 ml of water and oxidize organic matter by adding 10 ml of potassium permanganate solution and boiling for 2 min to 3 min. Add more of potassium permanganate solution if a deep purple colour does not persist. Boil for 5 min. Then destroy the excess permanganate and precipitated manganese dioxide by adding sulphurous acid solution, drop by drop until the solution is clear.

**9.3.2** Boil for 5 min. Cool the solution to 70 °C to 80 °C and add 5 g of ammonium nitrate. Add 20 ml of ammonium molybdate solution in small portions, while swirling the flask. Close the flask with the rubber stopper, shake vigorously for 5 min and allow to stand at room temperature for 1 h. Filter the precipitate through a thick pad of filter paper pulp prepared on a perforated disc in a funnel and wash the flask and the precipitate three times with dilute nitric acid and then wash five times with potassium nitrate wash solution. Continue washing the paper and the precipitate with potassium nitrate wash solution until free of acids.

**9.3.3** Transfer the pad with the precipitate back to the flask in which phosphorus was precipitated. Add 25 ml of water and add known excess of sodium hydroxide solution with stirring until all the yellow precipitate has dissolved and the solution is colourless. Add few millilitres of sodium hydroxide solution in excess and titrate with standard sulphuric acid using phenolphthalein indicator solution.

**9.3.4** Carry out a blank determination using the same quantity of sodium hydroxide solution as was added under 9.3.3 and titrate with standard sulphuric acid.

### 9.4 Calculation

$$\text{Phosphorus, percent} = \frac{(A - B) C \times 0.135}{D}$$

where

*A* = volume in ml of the standard sulphuric acid solution required to titrate the blank;

*B* = volume in ml of the standard sulphuric acid solution required to neutralize the excess sodium hydroxide solution;

*C* = normality of the standard sulphuric acid; and

*D* = mass, in g, of the sample taken.

## 10 DETERMINATION OF IRON BY THE DICHROMATE (VOLUMETRIC) METHOD

### 10.1 Outline of the Method

Iron is precipitated as hydroxide from the solution of the sample and dissolved in hydrochloric acid. To the boiling solution, stannous chloride is added in slight excess to reduce iron. The unused stannous chloride is destroyed by mercuric chloride and the reduced iron titrated with standard dichromate solution using sodium diphenylamine sulphonate as indicator.

### 10.2 Reagents

**10.2.1 Dilute Hydrochloric Acid** — 1 : 1 (v/v)

**10.2.2 Ammonium Chloride** — solid

**10.2.3 Concentrated Ammonium Hydroxide** — 20 percent

**10.2.4 Ammonium Chloride Solution** — 10 percent (w/v)

**10.2.5 Stannous Chloride Solution**

Dissolve, by heating, 60 g of pure stannous chloride in 400 ml of concentrated hydrochloric (specific gravity, 1.16) and 600 ml of water until the solution is complete. Cool and add a few pieces of granulated tin and preserve the solution in an air-tight amber-coloured bottle to prevent oxidation.

**10.2.6 Mercuric Chloride Solution**

Prepare a saturated solution of mercuric chloride in water.

**10.2.7 Sulphuric-Phosphoric Acid Mixture**

Add slowly 150 ml of concentrated sulphuric acid (specific gravity 1.84) to 700 ml of water with continuous stirring. Add to this 150 ml of syrupy phosphoric acid (85 percent). Destroy the oxidizable impurities by adding potassium permanganate solution (0.1 N) dropwise until the pink colour of permanganate persists and cool the solution.

**10.2.8 Sodium Diphenylamine Sulphonate Indicator Solution**

Dissolve 0.32 g of barium diphenylamine sulphonate in 100 ml of hot water. Add 0.5 g of the sodium sulphate, stir and filter off the precipitate of barium sulphate. Store in a dark-coloured bottle.

**10.2.9 Standard Potassium Dichromate Solution** — 0.1 N. Dry pure potassium dichromate (AR quality) in an oven at 105 °C to 110 °C for one and a half

hours. Cool in a desiccator and transfer carefully through a funnel exactly 4.9035 g to 1 litre volumetric flask, 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.

### 10.3 Procedure

**10.3.1** Transfer 5 g of the accurately weighed sample in a 400 ml beaker and add 50 ml of dilute hydrochloric acid and dissolve it slowly. Dilute the solution to 150 ml to 200 ml and add 5 g of ammonium chloride. Add concentrated ammonium hydroxide in slight excess until the iron is precipitated. Boil gently for few min. Allow the precipitate to settle for a few min and filter while hot. Wash the beaker and precipitate, first with hot ammonium chloride solution and finally with hot water to remove most of the soluble salts. Place the original beaker under the funnel and dissolve the precipitate through the paper with 20 ml of hot dilute hydrochloric acid. Add the acid in several portions, washing alternately with hot water. Finally wash thoroughly with hot water.

**10.3.2** Evaporate the solution to 25 ml and wash down the sides of the beaker. Heat to boiling and add stannous chloride solution, dropwise, while swirling the beaker over a white background, until the yellow colour of the ferric chloride disappears. Keep the solution near the boiling point for the entire period of reduction. Add not more than two drops in excess of stannous chloride solution.

**10.3.3** Dilute the reduced solution to 100 ml with water and cool to room temperature. While stirring, add in one instalment 10 ml of mercuric chloride solution. At this stage, a silky white precipitate appears. If it fails to appear or if a blackish precipitate appears, repeat the test. If the precipitate is too much, add further 5 ml of mercuric chloride solution. Keep it for 2 min to 5 min.

**10.3.4** Add 15 ml of sulphuric-phosphoric acid mixture and dilute to about 200 ml. Add three to four drops of sodium diphenylamine sulphonate indicator solution and titrate it slowly with standard dichromate solution, stirring continuously until the green colour begins to darken. Continue the titration slowly until a drop of dichromate solution gives a permanent violet-blue colouration.

**10.3.5** Make a blank determination, following the same procedure and using the same amount of all the reagents.

## 10.4 Calculation

$$\text{Iron, percent} = \frac{(A - B) C \times 5.585}{D}$$

where

*A* = volume in ml of the standard potassium dichromate solution consumed to titrate the sample;

*B* = volume in ml of the standard potassium dichromate solution consumed in blank titration;

*C* = normality of the standard potassium dichromate solution; and

*D* = mass, in g, of the sample taken.

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

### 11.1 Outline of the Method

The sample is heated to combustion at a high temperature (950 °C to 1 000 °C) in a stream of pure oxygen and the carbon is converted to carbon dioxide. The carbon dioxide, carried by oxygen, is passed through and absorbed by soda asbestos in a tared bulb, the increase in mass of which is proportional to the quantity of carbon dioxide formed.

### 11.2 Reagents

**11.2.1 Oxygen** — 99.5 percent purity free from carbonaceous matter

**11.2.2 Anhydrous Magnesium Perchlorate** [Mg(ClO<sub>4</sub>)<sub>2</sub>]

**11.2.3 Flux** — Lead dioxide, analytical reagent grade.

### 11.2.4 Manganese Dioxide

If a suitable chemical active grade is not available, it may be prepared as follows:

- a) To prepare about 50 g of manganese dioxide, dissolve in a 4 litre beaker, 200 g of manganous sulphate (MnSO<sub>4</sub>·4H<sub>2</sub>O) in 2.5 litres of water. After making this solution clearly ammoniacal, add 1 litre of ammonium persulphate solution (225 g per

litre) freshly prepared, bring to boiling point. Continue boiling for 10 min and add ammonia solution as frequently as is necessary to maintain the solution ammoniacal. Allow the precipitate to settle;

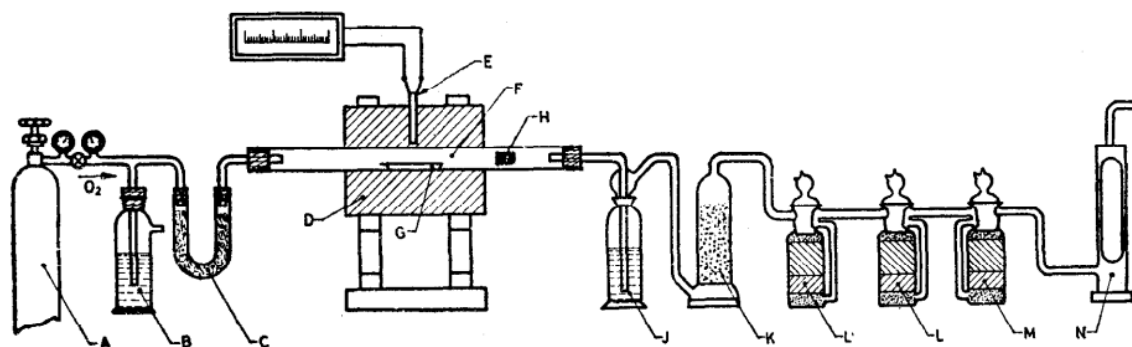
- b) If the supernatant liquid is not clear, or if the precipitate does not settle quickly, add 50 ml to 100 ml of ammonium persulphate solution and boil again for 10 min keeping the solution constantly ammoniacal;
- c) When precipitation appears to be complete, allow the manganese dioxide to settle completely, carefully siphon off the supernatant liquid and wash the precipitate by decantation with 3 litres or 4 litres of warm water in portions of 500 ml to 600 ml. Stir the manganese dioxide well in the water and allow to settle after each washing and before decantation. Finally wash twice in the same way with very dilute sulphuric acid;
- d) In the meantime, prepare a 15 cm diameter funnel fitted with a 5 cm filter disc filled with a thin layer of purified asbestos pulp (in place of the latter, it is also permitted to use a porcelain funnel of the Buchner type);
- e) After the last washing, transfer the manganese dioxide into the filter and wash with warm water until it is free from sulphate ions. Then place this on a porcelain dish and dry it in an oven at 105 °C; and
- f) Grind the manganese dioxide in a mortar so that it will pass through a sieve with apertures of 0.8 mm and dry again completely at 105 °C.

**11.2.5 Soda Asbestos** — Asbestos impregnated with sodium hydroxide, in granules of about 2 mm diameter. Avoid contact with air.

### 11.3 Apparatus

The apparatus consists of a source of oxygen and the unit for purifying it, the furnace with the combustion tube, the purification train and the carbon dioxide absorption system. These different parts, which are joined together with connecting tubes forming an air-tight seal, are shown in Fig. 1.





- A Source of oxygen (11.2.1) with pressure regulating valve;
- B Mercury valve;
- C Unit for drying and purifying the oxygen, containing anhydrous magnesium perchlorate (11.2.2) and soda asbestos (11.2.5) separated by glass wool (diameter of tubes 25 mm, height 100 mm, approximately) connected by tubing;
- D Wire-wound or resistor rod furnace, made of carborundum or metal and capable of a temperature for combustion up to 1 000 °C;
- E Thermocouple for measuring the temperature. The tip of the thermocouple protected by a sheath is placed near the external surface of the combustion tube. The relation between the internal tube temperature and the pyrometer reading should be established;
- F Combustion tube made of refractory material which is not porous at the test temperature, internal diameter 20 mm to 30 mm and at least 650 mm long so that the ends of the tube remain cold during combustion;
- G Boat made of refractory material (length 80 mm to 100 mm; width 12 mm to 14 mm, depth 8 mm to 9 mm), calcined in a stream of oxygen at the temperature of use;
- H Plug of calcined asbestos wool or quartz wool to filter the gas;
- J Washing bulb containing manganese dioxide. When analyzing samples of high sulphur content, it is preferable to use two washing bulbs of manganese dioxide or one washing bulb of manganese dioxide and one of chromic/sulphuric acid;
- K Drying bulb containing anhydrous magnesium perchlorate;
- L Weighed absorption bulbs for absorbing the carbon dioxide, containing soda asbestos (11.2.5) and a certain amount of anhydrous magnesium perchlorate (11.2.2) to trap the water which forms during absorption of the carbon dioxide. The total mass of each absorption bulb ready for use (see Fig. 2) should not exceed 100 g;
- M Unweighed absorption bulb facing the opposite way to L; and
- N Flowmeter.

FIG. 1 COMBUSTION APPARATUS FOR DETERMINATION OF CARBON BY GRAVIMETRIC METHOD

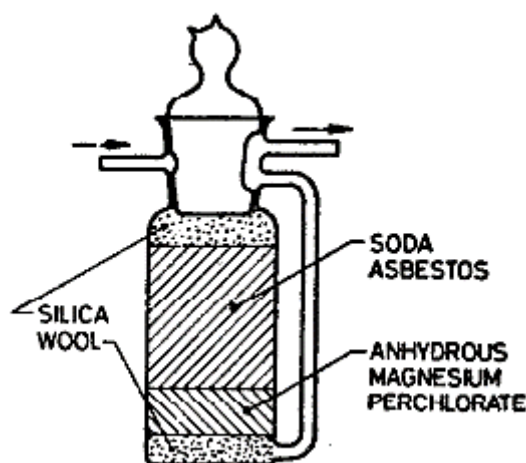


FIG. 2 ABSORPTION BULB

#### 11.4 Procedure

**11.4.1** After having verified the pressure tightness of the apparatus and the efficiency of the oxygen purification and having reached the required temperature within the range of 950 °C to 1 000 °C in the combustion zone of the furnace, allow oxygen to pass through the apparatus for 10 min to 15 min at the rate of 300 ml to 500 ml of gas per minute depending on the diameter of the tube used. Then disconnect the absorption bulbs and weigh them at the ambient temperature and replace them in position.

**11.4.2** Place 1 g of the sample in the form of very short chips having a thickness of a few tenths of a millimeter, in a boat. If necessary, add to the sample 1 g to 2 g of flux (**11.2.3**).

**11.4.3** Open the combustion tube at the end where the oxygen enters and using a rigid nickel wire, place the boat and the sample in the middle of the heated zone of the tube. Quickly close the tube and, after about 1 minute, pass through it a stream of oxygen at the rate of 300 ml to 500 ml per minute, depending on the diameter of the tube used. After about 1 min, when the combustion has ended, continue to pass oxygen through for another 15 min to 20 min so that the carbon dioxide is completely removed from the combustion tube and the purifying bulbs.

**11.4.4** Cut off the stream of oxygen, close the taps of the weighed absorption bulbs and remove the porcelain boat from the combustion tube. It is necessary to verify that the combustion has been efficiently completed by examining the fused mass in the boat removed from the furnace.

**11.4.5** Disconnect the absorption bulbs and weigh them at ambient temperature. The increase in mass represents the carbon dioxide absorbed.

**11.4.6** Carry out the blank test by the combustion of the boat in the presence of the quantity of flux used in the analysis, and carefully determine the mass of the absorption bulb. Where there is any doubt about the purity of the boat, this should be verified by the combustion in the boat of the amount of flux used in the analysis and carefully weighed, and a quantity of weighed electrolytic iron.

#### 11.5 Calculation

$$\text{Carbon, percent} = \frac{A - B}{C} \times 27.3$$

where

A = mass, in g, of carbon dioxide obtained from the combustion of the sample;

B = mass, in g, obtained from the blank test; and  
C = mass, in g, of the sample taken.

### 12 DETERMINATION OF TOTAL CARBON BY THE DIRECT COMBUSTION (VOLUMETRIC) METHOD (FOR CARBON CONTENT ≤ 0.1 PERCENT)

#### 12.1 Outline of the Method

The sample is burnt in a stream of pure oxygen and the resulting carbon dioxide and excess oxygen after removal of the contaminants, are collected in a specially jacketed burette and the carbon dioxide absorbed in alkali. On passing the excess oxygen back to the burette, the diminution in volume is read against a scale calibrated directly in percentages of carbon.

## 12.2 Reagents

**12.2.1 Oxygen** — 99.5 percent purity free from carbonaceous matter

**12.2.2 Concentrated Sulphuric Acid** — specific gravity 1.84 (conforming to IS 266)

**12.2.3 Soda Asbestos** — see **11.2.5**

**12.2.4 Asbestos Impregnated with Ferric Oxide** — Treat asbestos with a concentrated solution of ferric nitrate dry; and calcine at a 1 000 °C.

**12.2.5 Manganese Dioxide** — in granules to trap the combustion products of sulphur

**12.2.6 Potassium Hydroxide Solution** — containing 300 g of potassium hydroxide per litre

**12.2.7 Dilute Sulphuric Acid Solution** — 3 percent (v/v)

**12.2.8 Methyl Orange**

Dissolve 0.05 g of methyl orange in 100 ml of alcohol.

**12.2.9 Flux** — Lead dioxide, analytical reagent grade.

## 12.3 Apparatus

**12.3.1** The apparatus consists of a source of oxygen and the unit for purifying it, the furnace with the combustion tube; the purification train and the carbon dioxide absorption system. These different parts, which are joined together with connecting tubes forming an air-tight seal, are shown in Fig. 3.

## 12.4 Procedure

**12.4.1** After having verified the pressure tightness of the apparatus, and reaching the temperature 950 °C to 1 000 °C in the combustion zone of the furnace, wash the combustion tube with a stream of oxygen, completely fill the special measuring burette *M* and the absorption receiver *N* with the respective liquids manipulating the levelling bottle *P* and tap *L* as appropriate is open. At this point, the tap *L* is closed and the tap on the bottle *P* is open.

### 12.4.2 Combustion

**12.4.2.1** Place 2 g of accurately weighed sample in the calcined porcelain boat. If necessary, add about 2 g of flux (see **12.2.9**). Open the combustion tube at the end where the oxygen enters and using a rigid nickel wire, place the boat and the sample in the

middle of the heating zone of the tube. Quickly close the tube and after about half a minute during which time the oxygen should be turned off, connect the tube with the measurement burette *M* by means of tap *L* and at the same time pass a stream of oxygen through the apparatus (liquid in the burette should descent slowly).

**12.4.2.2** The stream of oxygen should be regulated so that at the end of combustion there is enough space in the measurement burette to receive the carbon dioxide formed and also the excess oxygen required for completely removing the last traces of carbon dioxide from the combustion tube *F*, from the bulb *J*, and from the capillary coil *K*. When the level of the liquid in the burette *H* continuing its descent, comes near to zero of the scale turn the tap *L* which cuts off communication of burette *M* with the combustion tube *F*, stop the stream of oxygen, and remove the boat from the combustion tube. It is necessary to find out whether combustion has been duly effective, by examining the fused mass in the boat removed from the furnace.

### 12.4.3 Determination

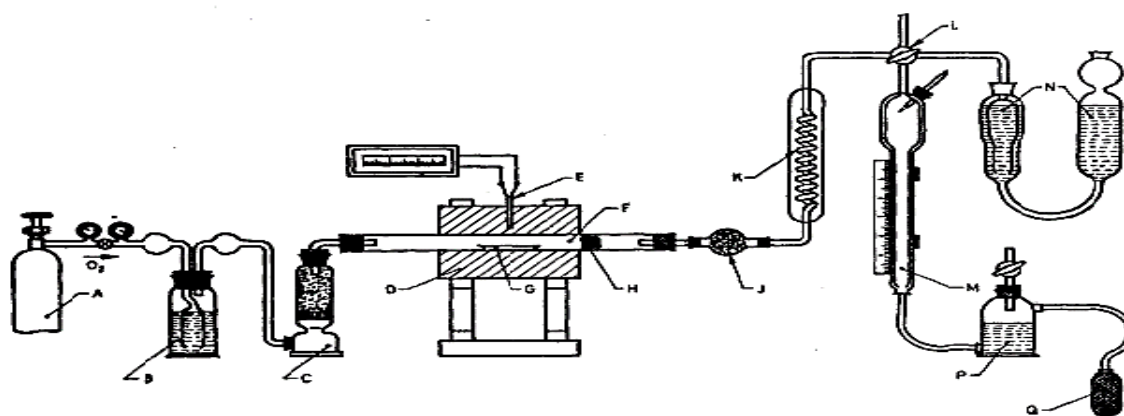
**12.4.3.1** After two min, the measuring liquid in the burette and in the measuring bottle *P* with the tap still open, should be brought to the same level, and the graduated scale should be moved so as to bring the zero to the level of the liquid.

**12.4.3.2** Then, by means of tap *L*, connect burette *M* with the absorption receiver *N*, close the tap on the levelling bottle *P*, and by means of the compression valve *Q*, slowly pass the gas into the absorption receiver *N*.

**12.4.3.3** Open the tap on the levelling bottle *P*, lower the latter, and bring back the gas into the measurement burette *M*.

**12.4.3.4** Recommence passing the gas into the potassium hydroxide solution in absorption receiver *N*, bring back all the gas into the measurement burette, close the stopcock end and, after obtaining the same level of the liquids, read on the scale the percentage carbon and the temperature of the gas correct to  $\pm 0.05$  °C.

**12.4.3.5** The burette is graduated to measure directly in percentage up to 1.5 percent carbon on the basis of 1 g sample taken. From the reading on the scale the percentage of carbon could be calculated on the basis of 2 g sample taken in **12.4.2.1**.



- A* Source of oxygen (12.2.1) with pressure regulating valve;
- B* Washing bottle containing concentrated sulphuric acid (12.2.2);
- C* Column containing soda asbestos (12.2.3).
- D* Wire-wound or resistor rod furnace, made of Carborundum or metal and capable of a temperature for combustion up to 1 350 °C;
- E* Thermocouple for measuring the temperature. The tip of the thermocouple, protected by a sheath, is placed near the external surface of the combustion tube. The relation between the internal tube temperature and the pyrometer reading should be established;
- F* Combustion tube made of refractory not porous at the test temperature, 20 mm to 30 mm and at least 650 mm long so) of the tube remain cold during combustion;
- G* Boat made of refractory material (length 80 mm to 100 mm, width 12 mm to 14 mm, depth 8 mm to 9 mm), calcined in a stream of oxygen at the temperature of use;
- H* Layer of asbestos impregnated with ferric oxide (12.2.4) in order to oxidize all the carbon into carbon dioxide;
- J* Glass bulb, filled with manganese dioxide granules (12.2.5) and quartz wool, to trap any sulphur combustion products and dust carried over by the stream of gas;
- K* Capillary coil, water cooled (inside diameter 1.5 mm);
- L* Tap used for connecting the coil *K* with the special calibrated burette *M*, or with the absorption receiver *N* or with the atmosphere;
- M* Special calibrated burette, cooled by a water jacket, with an enlarged portion at the top fitted with a thermometer capable of readings correct to 0.05 °C. The capacity of the burette should be about 400 ml for carbon contents up to 1.5 percent. The bottom of the burette is connected by a rubber tube to a levelling bottle *P*, on the side of the calibrated lower portion of the burette there is a scale capable of sliding along the burette itself;
- N* Absorption receiver with liquid trap, containing a solution of potassium hydroxide (12.2.6) used for absorbing the carbon dioxide;
- P* Levelling bottle, containing water, dilute sulphuric acid (12.2.7) coloured red with methyl orange (12.2.8) with tap and compression valve; and
- Q* Rubber compression valve.

FIG. 3 COMBUSTION APPARATUS FOR DETERMINATION OF CARBON BY VOLUMETRIC METHOD

**12.4.4 Blank Test**

Blank test should be carried out by combustion of a mass of metal of known carbon content in the presence of amounts of the normally used fluxes carefully weighed.

**13 DETERMINATION OF ALUMINIUM BY THE BENZOATE OXINATE (GRAVIMETRIC) METHOD****13.1 Outline of the Method**

Aluminium is precipitated from the solution of the sample as basic benzoate and dissolved in hydrochloric acid. It is then precipitated as hydroxyquinoline complex, dried and weighed as aluminium oxyquinolate.

**13.2 Reagents**

**13.2.1 Concentrated Hydrochloric Acid** — as in 7.2.2

**13.2.2 Ammonium Chloride** — solid

**13.2.3 Ammonium Hydroxide Solution** — 1 : 1 (v/v)

**13.2.4 Acetic Acid** — glacial

**13.2.5 Ammonium Benzoate Solution**

Dissolve 100 g of ammonium benzoate in warm water, add one milligram of thymol as a preservative and dilute to one litre.

**13.2.6 Benzoate Wash Solution** — to 100 ml of ammonium benzoate solution, add 900 ml of water, and 20 ml of glacial acetic acid.

**13.2.7 Ammoniacal Tartrate Solution**

Dissolve 30 g of ammonium tartrate in one litre of water containing 120 ml of ammonia.

**13.2.8 8-Hydroxyquinoline Solution**

Dissolve 50 g of 8-hydroxyquinoline in 120 ml of glacial acetic acid and dilute to one litre with water. Filter if necessary and keep in a dark-coloured bottle.

**13.3 Procedure**

**13.3.1** Transfer 2 g to 5 g of the accurately weighed sample to a 500 ml beaker, add 25 ml of water and dissolve by adding, in small portions 5 ml of concentrated hydrochloric acid for each 2 g of the sample. When dissolved, cool to room temperature and dilute to 100 ml. Add ammonium chloride (5 g per 1 g of sample) and add ammonium hydroxide solution drop by drop, until the precipitate that forms finally redissolves only very slowly; that is until nearly all of the free hydrochloric is neutralized.

**13.3.2** Add 1 ml of glacial acetic acid and 20 ml of ammonium benzoate solution. Heat to boiling, while stirring vigorously, and boil gently for five min. Filter on a Gooch crucible of medium porosity with the aid of suction. Wash the precipitate 8 to 10 times with hot benzoate wash solution, making no effort to transfer all the precipitate to the Gooch crucible.

**13.3.3** Return the precipitate from the Gooch crucible to the original beaker. Transfer most of the remainder precipitate by means of a stream of water. Dissolve the small portion that adheres to the crucible by washing with five 10 ml portions of hot ammoniacal tartrate solution; adding these washings to the precipitate in the beaker. Dilute to 150 ml to 200 ml. Heat the solution to 70 °C to 80 °C, add 25 ml of 8-hydroxyquinoline solution, and digest for 30 min without boiling. Filter on the same crucible transferring whole of the precipitate to the crucible and wash eight times with warm water.

**13.3.4** Dry the precipitate for 2 h at 120 °C to 130 °C, cool and weigh as aluminium oxyquinolate,  $\text{Al}(\text{C}_9\text{H}_6\text{ON})_3$ .

**13.4 Calculation**

$$\text{Aluminium, percent} = \frac{A \times 5.87}{B}$$

where

$A$  = mass, in g, of aluminium oxyquinolate; and

$B$  = mass, in g, of the sample taken.

## ANNEX A

*(Foreword)*

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This Indian Standard has been developed from Doc No.: MTD 34 (21315).

### Amendments Issued Since Publication

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