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“जानने का अधिकार, जीने का अधिकार”

Mazdoor Kisan Shakti Sangathan

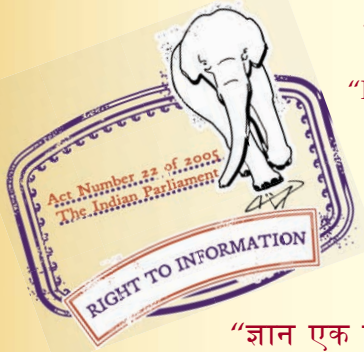
“The Right to Information, The Right to Live”

“पुराने को छोड़ नये के तरफ”

Jawaharlal Nehru

“Step Out From the Old to the New”

IS 1473 (2004): Methods of Chemical Analysis of Manganese Ores [MTD 13: Ores and Raw Materials]



“ज्ञान से एक नये भारत का निर्माण”

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“Invent a New India Using Knowledge”



“ज्ञान एक ऐसा खजाना है जो कभी चुराया नहीं जा सकता है”

Bhartrhari—Nitiśatakam

“Knowledge is such a treasure which cannot be stolen”

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भारतीय मानक
मैंगनीज अयस्क रासायनिक विश्लेषण की पद्धतियाँ
(पहला पुनरीक्षण)

Indian Standard
METHODS OF CHEMICAL ANALYSIS OF
MANGANESE ORES
(*First Revision*)

ICS 73.060.20

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BUREAU OF INDIAN STANDARDS
MANAK BHAVAN, 9 BAHADUR SHAH ZAFAR MARG
NEW DELHI 110002

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 Ores, Minerals and Allied Materials for Metallurgical Industry Sectional Committee had been approved by the Metallurgical Engineering Division Council.

India has extensive deposits of manganese ore, a vital raw material in steel manufacture; and is at present the second largest producer of this ore in the world. Most of the principal steel producing countries, such as USA, UK, France, Japan, etc, are deficient in this mineral and India is one of the countries on which they depend for the supplies of this ore. The value of the ore depends to a great extent on the chemical composition, the value falling sharply with the decrease in manganese content below a certain minimum; impurities like iron, phosphorus, silica and alumina should not exceed certain limits. Therefore, the correct analysis of the elements is required.

The Committee responsible for the formulation of this standard felt the need of incorporation of atomic absorption method in addition to conventional method for the determination of Si, Al, Ti, Fe, Ca, Mg, Cu, Pb, Zn, Co, Cr, V, Ba and K.

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*)'.

Indian Standard

METHODS OF CHEMICAL ANALYSIS OF MANGANESE ORES

(First Revision)

1 SCOPE

This standard prescribes the following methods for determination of various elements in manganese ores:

- a) Chemical analysis by gravimetric and volumetric method, and
- b) Atomic absorption method.

The gravimetric and volumetric methods are suitable for determination of silica, barium oxide, manganese, iron, phosphorus, sulphur, alumina and other elements in manganese ores and concentrates.

The atomic absorption method can be used for the determination of Si, Al, Ti, Fe, Ca, Mg, Cu, Pb, Zn, Co, Cr, V, Ba and K, in the following ranges and composition:

SiO ₂	0.25	percent	to	25	percent
Al ₂ O ₃	0.12	percent	to	25	percent
TiO ₂	0.20	percent	to	2.5	percent
Fe ₂ O ₃	50	ppm	to	22.5	percent
CaO	20	ppm	to	10	percent
MgO	5	ppm	to	10	percent
Na ₂ O	5	ppm	to	500	ppm
K ₂ O	5	ppm	to	500	ppm
Cu	10	ppm	to	0.25	percent
Pb	25	ppm	to	0.25	percent
Zn	5	ppm	to	0.25	percent
Cr	10	ppm	to	0.25	percent
Co	10	ppm	to	0.25	percent
V	250	ppm	to	0.25	percent

2 REFERENCES

The following standards 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 the standards indicated below:

IS No.	Title
264 : 1976	Nitric acid (<i>second revision</i>)
265 : 1993	Hydrochloric acid (<i>fourth revision</i>)
266 : 1993	Sulphuric acid (<i>third revision</i>)
323 : 1959	Specification for rectified spirit (<i>revised</i>)

IS No.

Title

1070 : 1992	Reagent grade water (<i>third revision</i>)
1449 : 1976	Methods of sampling of manganese ore (<i>first revision</i>)
7659	Reagents and standard solutions for use in chemical analysis of metals, ores and minerals : Part 1 Volumetric solution
(Part 1): 1975	
11895 : 1986	Classification of manganese ore, ferruginous manganese ore, silicious manganese ore and manganiferrous iron ore

3 REAGENTS

All reagents used shall be pure chemicals of analytical reagents grade, which do not contain impurities which would affect the analytical results.

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

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

Reagents which are poisonous shall be properly labelled and shall be allowed to be handled by the authorized chemists with proper instructions. The concentrations of solutions are often expressed in the following form:

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

4 APPARATUS

4.1 Weighing shall be carried out using an analytical balance with a constant sensitivity. It shall be capable

of weighing 100 or 200 g and shall be able to read a difference of 0.4 mg.

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

The texture of filter paper shall be of certified graded quality (for example, marked by Whatman International Limited, England), so also the filtering equipment (such as graded sintered crucibles or standard laboratory glass micro-fibre filter) shall be of certified graded quality.

4.2 Sample Used for Chemical Analysis

The laboratory sample prepared for the purpose of chemical analysis (*see* IS 1449) shall be pulverized preferably to pass 100 micron standard sieve. The pulverized sample shall be mixed thoroughly by rolling on a non-absorbant paper and spread uniformly. From this a sufficient quantity shall be taken as representative sample and transferred to a glass or stainless steel petri dish, closed with a cover and dried in a hot air oven at $105 \pm 5^\circ\text{C}$ for about 2 h or more and then cooled in a desiccator (containing calcium chloride, calcined at 700° to 800°C). This dried sample shall be used for the purpose of chemical analysis, and is termed as a test portion. For ores which are known to be of hygroscopic nature, the sample (ground to ~ 100 microns) shall be analyzed on as received basis and the results reported on dry basis (that is dried at $105 \pm 5^\circ\text{C}$). For this purpose, the hygroscopic moisture shall be determined simultaneous with the analysis and correction factor found out as follows, shall be applied for each determination for reporting on dry basis.

5 PROCEDURE

Dry a glass petri dish with cover in an air oven at $105 \pm 5^\circ\text{C}$, cool in a desiccator and weigh. Weigh 5 g of the ground sample (~ 100 micron size), and transfer it to the petri dish. Close the cover and heat it in the air oven at $105 \pm 5^\circ\text{C}$ to a constant mass (nearly 2 h of drying may be enough). Cool in a desiccator and weigh. From the loss in mass, calculate the correction factor K as follows (correct to four places of decimals). All weights shall be recorded to nearest 0.1 mg.

$$K = \frac{100}{100 - A}$$

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

where

m_1 = mass, in g, of the empty petri dish with cover (dried);

K = correction factor;

m_2 = mass, in g, of the petri dish with sample and cover after drying; and

m = mass, in g, of the sample, before drying.

5.1 Number of Test Portions

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

5.2 Test

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

5.3 Check Test

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

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

5.4 Expression of the Analytical Values

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

- a) Elements to be expressed to two places of decimal : total manganese, manganese dioxide, manganous oxide, silica, alumina, barium oxide, ferric oxide, iron, combined water.

Loss on ignition, matter insoluble in acid, calcium and magnesium oxides, titanium and titanium oxide.

- b) Elements to be expressed to three places of decimal: Phosphorous, phosphorous pentoxide, sulphur, sulphur trioxide, sodium

oxide, potassium oxide, and minor elements such as copper, lead, zinc, arsenic, nickel, vanadium, etc.

In case of 1 percent or more of phosphorous and sulphur and in the case of 0.1 percent or more of minor elements, analytical values shall be expressed to two places of decimal.

5.5 Test Report

The final test report shall include the following information:

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

6 DETERMINATION OF SILICA BY THE GRAVIMETRIC METHOD

6.1 Outline of the Method

The sample is decomposed with hydrochloric acid and taken to fumes with sulphuric acid and filtered. The residue is extracted with ammonium acetate to remove lead, ignited and then fused with sodium carbonate. The fused mass is extracted with hydrochloric acid and silica, in the residue, determined by hydrofluorization. The general range of silica, applicable, for this method, shall be 1 to 15 percent (*m/m*).

6.2 Reagents

6.2.1 Concentrated Hydrochloric Acid, sp. gr. 1.16 (*see* IS 265).

6.2.2 Dilute Sulphuric Acid, 1:1 (*v/v*).

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

6.2.4 Ammonium Acetate Solution — 20 percent (*w/v*).

6.2.5 Dilute Nitric Acid, 1:1 (*v/v*).

6.2.6 Sodium Carbonate, anhydrous.

6.2.7 Dilute Hydrochloric Acid, 1:1 (*v/v*).

6.2.8 Hydrofluoric Acid, 40 percent.

6.3 Procedure

6.3.1 Transfer 2.5 g of the accurately weighed test sample to a 400 ml beaker and digest with 30 ml of concentrated hydrochloric acid. Cover the beaker with a watch-glass and heat the solution on a hot-plate. Wash the watch-glass and sides of the beaker with a small quantity of water, and concentrate the solution. Add 20 ml of dilute sulphuric acid and evaporate to fumes. Cool the fumed mass and add about 200 ml of water. Heat the solution to boiling. Allow to cool and settle. Filter the residue and wash it with lead-acid solution. Preserve the filtrate.

6.3.2 The residue, on the filter paper, consists of siliceous material from the sample together with sulphates of barium and lead, titania and undecomposed manganese ore. Extract the residue with hot ammonium acetate solution to remove lead sulphate and preserve the extract for the determination of lead. Incinerate the filter paper completely, cool, add a few drops of dilute nitric acid and a drop or two of dilute sulphuric acid and evaporate on a hot plate until fuming of sulphuric acid nearly ceases. Heat the crucible at about 600°C placing it inside a larger crucible with an air space between the two.

6.3.3 Fuse the residue in a platinum crucible with six to eight times its weight of sodium carbonate. Digest the cooled mass with hot water and acidify with dilute hydrochloric acid. Boil the solution for few minutes for the removal of carbon dioxide and add carefully 20 ml of dilute sulphuric acid. Evaporate to dense fumes, take up the mass with water and keep for an hour. Filter, add the filtrate to the solution preserved under **6.3.1** and preserve the combined solution. Ignite the final residue in a platinum crucible at 900° to 950°C and weigh. Add sufficient dilute sulphuric acid to moisten the residue and add carefully 10 to 15 ml of hydrofluoric acid. Evaporate to dryness and ignite the residue. Weigh the platinum crucible again. Repeat the hydrofluoric acid treatment till constant weight is obtained. The loss in weight of the residue represents the weight of silica in the sample. Preserve the residue. The test shall be carried out in duplicate.

Permissible tolerance between parallel determinations shall have to be added, after conducting inter-laboratory tests.

6.4 Calculation

$$\text{Silica, percent} = \frac{A \times 100 \times K}{B}$$

where

A = loss in weight, in g, of the final residue,

B = weight, in g, of the sample taken, and

K = hygroscopic moisture factor of the expression of silica on dry basis (if the dried sample is directly taken for the test, then $K=1$).

Mean, silica, percent (m/m) of the duplicate tests shall be reported.

7 DETERMINATION OF BARIUM OXIDE BY THE GRAVIMETRIC METHOD

7.1 Outline of the Method

The residue, left after silica determination, is fused with potassium bisulphate, extracted with sulphuric acid, and filtered. The residue is then ignited and weighed as barium sulphate. The general range of barium oxide applicable for this method shall be >0.1 percent (m/m).

7.2 Reagents

7.2.1 *Potassium Bisulphate*, solid.

7.2.2 *Dilute Sulphuric Acid*, 1 : 1 (v/v).

7.3 Procedure

Fuse the residue reserved under 6.3.3 in a platinum crucible with six times its weight of potassium bisulphate and extract with dilute sulphuric acid. Add the filtered extract to the combined solution reserved under 6.3.3. Concentrate, if necessary, and transfer to a 500 ml graduated flask. Cool, make up to the mark and mix well. Treat this solution as the main solution for the estimation of manganese, iron, alumina, titania, calcium oxide, magnesium oxide, copper and arsenic. Wash the residue with water until nearly free from acid, dry and ignite at 600° to 650°C and weigh as barium sulphate (BaSO_4). The test shall be carried out in duplicate.

Permissible tolerance between parallel determinations shall be added, after conducting the necessary tests.

7.4 Calculation

$$\text{Barium oxide, percent} = \frac{A \times 0.657 \times K}{B} \times 100$$

where

A = weight, in g, of barium sulphate;

B = weight, in g, of the sample taken; and

K = conversion factor of the expression of barium oxide on dry basis (if the dried sample is directly taken for the test, then $K=1$)

Calculate the mean barium oxide, percent (m/m) from duplicate tests.

8 DETERMINATION OF MANGANESE BY THE BISMUTHATE (REFEREE) METHOD

8.1 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 titrated with standard ferrous ammonium sulphate solution.

8.2 Reagents

8.2.1 *Dilute Aluminium Hydroxide*, 1 : 3 (v/v).

8.2.2 *Concentrated Nitric Acid*, sp.gr.1.42 (see IS 264).

8.2.3 *Sodium Bismuthate* — The chemical shall not contain : less than 70 to 80 percent active oxygen, as calculated for NaBiO_3 , more than 0.002 percent chlorine ions or more than 0.001 percent manganese.

8.2.4 *Dilute Sulphuric Acid*, 5 : 95 (v/v).

8.2.5 *Standard Ferrous Ammonium Sulphate Solution (0.1 N)* — Dissolve 39.2 g of ferrous ammonium sulphate $\{\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}\}$ crystals in cold dilute sulphuric acid (5:95) and make up to one litre with this acid. Standardize against standard potassium permanganate solution (see 8.2.7).

8.2.6 *Nitric Acid*, 3 : 97 (v/v) — Shall be free from oxides of nitrogen. The oxides of nitrogen shall be removed by passing a current of oxygen or air through the concentrated nitric acid (sp. gr. 1.40) until there is a complete decolourization of the latter.

8.2.7 *Standard Potassium Permanganate Solution* — 0.1 N. Dissolve 3.2 g of potassium permanganate in one litre of water. Let it stand in the dark for two 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 sodium oxalate (AR) by weighing 0.134 g of the salt, dissolving it in 250 ml of dilute sulphuric acid (5:95) and titrating against the permanganate solution at 55° to 60°C to a faint pink end-point. Adjust the strength of permanganate solution such that 0.134 g of sodium oxalate requires exactly 20 ml of the permanganate solution.

8.3 Procedure

Weigh accurately 2.5 g of ore, into a 250 ml conical beaker, dissolve it by heating in 50 ml nitric acid 1:3 (v/v), while covering it with watch-glass. Carefully add, drop by drop, 30 percent hydrogen peroxide, until the attack is complete. Filter the solution through a medium texture filter paper, into 250 ml volumetric flask. Wash the filter several times with nitric acid 1:3 (v/v).

Incinerate the filter paper into a platinum crucible and then ignite. Cool, add a few drops of sulphuric acid and 10 ml hydrofluoric acid, and evaporate carefully to dryness. Fuse it with 2 g sodium carbonate, extract the fused mass with nitric acid, 1:3 (v/v) and add the solution to the mass filtrate in the volumetric flask, dilute with water up to the mark and mix well. Transfer an aliquot so as to represent 0.25 g of the ore.

8.3.1 Transfer an aliquot from the main solution of the sample preserved under 7.3 so as to represent 0.5 to 0.25 g of the ore. Dilute with water to 100 ml and neutralize with dilute ammonium hydroxide until a persistent precipitate forms. Just dissolve the precipitate with concentrated nitric acid and add 40 ml of the acid in excess. In order to destroy the organic matter and to oxidize other reducers, add to the solution, which has been heated to boiling, one gram of sodium bismuthate in small portions. Boil for a few minutes and dissolve the precipitated manganese dioxide by the dropwise addition of ferrous ammonium sulphate solution. Boil for three minutes to expel the oxides of nitrogen and cool to 10° to 15°C.

8.3.2 Add 6 to 8 g of sodium bismuthate to the cooled solution and stir vigorously for 2 min. Dilute with 100 ml of cold water and filter immediately through calcined asbestos pad. The filtrate should be absolutely transparent. Wash the filter and the residue with cold dilute freshly boiled nitric acid until washings are entirely colourless. Add measured excess of standard ferrous ammonium sulphate solution, stir, and titrate the excess with the standard permanganate solution to the appearance of faint pink colour.

8.3.3 Run a blank through all stages of the procedure, using the same amount of ferrous ammonium sulphate solution as added in the test under 8.3.2 and titrate with standard permanganate solution. Carry out the test in duplicate. The volume in millilitres of standard potassium dichromate consumed in the test shall be recorded as *B* (see 8.4).

8.4 Calculation

$$\text{Manganese, percent} = \frac{(A - B) \times 0.001}{C} \times 100$$

where

A = volume, in ml, of the standard permanganate solution (0.1 N) required to titrate the blank;

B = volume, in ml, of the standard permanganate solution (0.1 N) required to titrate the excess ferrous ammonium sulphate solution; and

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

It is preferable to carry out the standardization of

potassium permanganate, against a certified standard sample of manganese ore following the above procedure.

NOTE — The asbestos used in the titration should not contain organic matter or any matter that may react with potassium permanganate. For this purpose, split the asbestos into fibers, treat while heating with hydrochloric acid and wash thoroughly with distilled water. Then heat it with nitric acid [1:3 (v/v)] and wash with water to remove chlorine ions. Dry and heat to a temperature of 500° to 600°C.

Calculate the mean Manganese, percent (*m/m*) from the duplicate tests, if they meet the permissible tolerance. Otherwise repeat the tests.

8.5 Permissible Tolerance Between Parallel Determination

Mn, percent (<i>m/m</i>)	Permissible Tolerance Between Parallel Tests, percent (<i>m/m</i>)
Up to 20	0.20
Over 20 to 40	0.30
Over 40	0.40

NOTE — This method is generally applicable to manganese ores/concentrates in the range of manganese contents specified under IS 11895 'Classification of manganese ore, ferruginous manganese ore, silicious manganese ore and magnaniferrous iron ore.'

9 DETERMINATION OF MANGANESE BY THE VOLHARD'S METHOD

9.1 Outline of the Method

This method is based on the oxidation of divalent manganese with potassium permanganate in a hot (not less than 80°C) solution neutralised with zinc oxide and containing a little excess of the latter. The end point is indicated by the persistent pink colour.

9.2 Reagents

9.2.1 Hydrochloric Acid, sp. gr. 1.16.

9.2.2 Nitric Acid, 1 : 1 (v/v).

9.2.3 Hydrofluoric Acid, 40 percent (v/v).

9.2.4 Sulphuric Acid, 5 : 95 (v/v).

9.2.5 Sodium Oxalate, 99.9 percent or more.

9.2.6 Potassium Bisulphate

9.2.7 Zinc Oxide Emulsion — free from impurities that may react with potassium permanganate under conditions of analysis. Add 20 g of zinc oxide, heated to 800°C to about 100 ml of hot water and mix well.

9.2.8 Standard Potassium Permanganate (0.1 N) — Dissolve 3.2 g of potassium permanganate in one litre of water. Let it stand in the dark for two weeks and filter without washing through a fritted glass crucible

of fine porosity or through glass wool, avoiding contact with rubber or other organic material. Store in an amber-coloured glass-stoppered bottle.

NOTE — 1 ml 0.1(N) $\text{KMnO}_4 = 0.001\ 648\ \text{g Mn}$.

9.3 Standardization of Potassium Permanganate Solution (0.1 N)

9.3.1 Against Standard Certified Sample of Manganese Ore — To determine the factor 'F' of potassium permanganate solution expressed in grams of manganese, take a standard certified sample of manganese ore, having approximately the same manganese content as that of the sample being analysed, and take it through all the stages of the analysis, given in the subsequent clauses. Find out the factor *F* from the formula:

$$F = \frac{A \times G}{V \times 100}$$

where

F = factor of potassium permanganate;

A = manganese content, percent, in the standard sample of ore;

G = mass, of the standard sample of ore in gram; and

V = number of millilitres of potassium permanganate solution used in the titration of manganese contained in the standard sample

9.3.2 Against Sodium Oxalate (as an Alternate Method)

9.3.2.1 Weigh accurately 0.134 g of sodium oxalate, dried to constant mass at a temperature of 110° to 120°C, into a 500 ml beaker. Add to it 250 ml of sulphuric acid (5:95 v/v), heat the solution to a temperature of 80°C and then titrate with the potassium permanganate solution until a faint permanent pink tinge is reached.

9.3.2.2 The factor 'F' of potassium permanganate, expressed in grams of manganese, shall be calculated from the following formula:

$$F = \frac{G \times 0.245\ 985}{V}$$

where

F = factor of potassium permanganate;

G = mass of sodium oxalate in grams 0.245 985 is the conversion factor for potassium solution, expressed as sodium oxalate, in terms of manganese; and

V = number of millilitres of potassium permanganate solution used for titrating the sodium oxalate.

The factor 'F' shall be obtained with three test samples

of sodium oxalate; the mean of two closely coinciding results being taken as the final result, correct to six decimal places.

9.3.2.3 It is advisable to check periodically the factor 'F' of potassium permanganate solution.

9.4 Procedure

9.4.1 Take separately 2.5 g of the sample, weighed, nearest to 0.1 mg in a 250 ml conical flask, add 25 ml hydrochloric acid and a few drops of nitric acid and heat, till most of the ore goes into solution. Filter through a medium texture filter paper, such as Whatman No. 40, wash the residue with hydrochloric acid 1:1 (v/v) till all the orange stains are washed off and finally with hot water. Collect the filtrate and washings in 250 ml volumetric flask. Place the filter paper in a platinum crucible and incinerate the filter paper by gradual heating and ignite. After cooling, moisten the residue with a few drops of sulphuric acid 1:1 (v/v) and 10 ml hydrofluoric acid. Gently heat and volatilize silica and sulphuric acid. Cool, fuse the residue with 2 g potassium bisulphate and extract with 25 ml hydrochloric acid 1:1 (v/v). Mix with the filtrate already collected in 250 ml volumetric flask. Make up to 250 millilitres in the volumetric flask and mix well. Transfer 2.5 millilitres of the solution from the flask for each test.

9.4.2 Collect the aliquots obtained in 9.4.1 equivalent to 0.25 g of ore, into 1 000 ml Erlenmeyer flask and boil to remove free chlorine (important). Dilute with hot water to about 600 ml, stirring the solution for a while, carefully add in small portions zinc oxide emulsion till there is a slight white precipitate of zinc oxide at the bottom of the flask.

9.4.3 Heat the solution in the flask to boiling and while rotating it vigorously, titrate with the standard solution of potassium permanganate, added in small portions. After adding each portion shake the contents of the flask 2 to 3 times. Place the flask obliquely on a support and observe the colour of the supernatant liquid. After the appearance of the pink tint, vigorously shake the contents of the flask once more (if the solution has cooled down, heat it to a temperature of 90° to 95°C). If after heating, the pink tint is retained, the first tentative titration may be considered finished.

9.4.4 The second and more precise titration is carried out by allowing to pour, all at once, the standard potassium permanganate up to a quantity 0.5 ml less than was established by the first titration, then go on adding the solution in portions of 0.1 to 0.2 ml shaking vigorously each time until pink colour appears which remains unchanged for 1 min.

9.4.5 Then carry out the titration of the third test sample of the ore.

9.4.6 The volume of standard potassium permanganate used in the titration is measured to an accuracy of 0.05 ml, after a lapse of 2 to 3 min from the end of the titration, so as to give the solution time to drain down the sides of the burette.

9.5 Blank Test

Excluding only the sample used for the test, carry out, the procedure, using the same quantities of reagents in accordance with 9.4. Record the volume of standard potassium permanganate as the blank. Record it as V_2 ml.

9.6 Calculation

The percentage of total manganese (m/m) is calculated as follows:

$$\text{Mn (percent)} = \frac{F \times (V_1 - V_2) \times 100 \times K}{G}$$

where

F = factor of potassium permanganate in grams of manganese (see 9.3.2.2);

V_1 = number of millilitres of standard potassium permanganate used in the second or third titrations (see 9.4.4);

V_2 = millilitres of potassium permanganate solution consumed in the blank test (see 9.5);

G = mass of sample of ore in grams;

K = hygroscopic moisture content of the test sample. If dried test sample is used directly, then $K = I$.

Calculate mean Mn, percent (m/m) of the duplicate tests, if they meet the permissible tolerance.

9.7 Permissible Tolerance

The permissible tolerance for parallel determination is given in the table below:

Mn, percent (m/m)	Permissible Tolerance Between Parallel Tests, percent (m/m)
Up to 20	0.20
Over 20 to 40	0.30
Over 40	0.40

10 DETERMINATION OF MANGANESE DIOXIDE BY THE OXALATE METHOD

10.1 This method applies to the overall range of manganese ores/concentrates.

10.1.1 Outline of the Method

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

10.2 Reagents

10.2.1 Standard Sodium Oxalate Solution (0.1 N)

Weigh 6.7 g of pure (99.9 percent or more) sodium oxalate, dried at 105° to 110°C and dissolve in 300 ml water. Dilute to one litre in a volumetric flask and mix well.

10.2.2 Sulphuric acid, 20 percent (v/v).

10.2.3 Standard Potassium Permanganate (0.1 N), for preparation and standardization (see 9.2.8 and 9.3).

10.3 Procedure

10.3.1 For ores containing up to 30 percent manganese dioxide, weigh 0.5 g of the test sample; for ores containing more than 30 percent manganese dioxide, weigh 0.25 g of the test sample.

10.3.2 The test sample shall preferably be ground to 75 micron sieve. The factor K , for hygroscopic moisture, if required, shall be determined on the test sample ground to 75 micron size.

10.3.3 Transfer the required mass of accurately weighed test sample, into 500 ml Erlenmeyer flask, add 50 ml of the standard sodium oxalate solution and 50 ml of sulphuric acid to the sample. Insert a funnel into the mouth of the Erlenmeyer flask and heat on a water bath (at about 90°C) with occasional shaking till the residue turns colourless, free from any black ore particles wash the funnel carefully collecting all washings into the flask. Dilute the solution to approximately 200 ml with hot water and immediately titrate it with standard potassium permanganate, while keeping the contents at 60° to 70°C, till the last drop gives a persistent faint pink end-point. Carry out the test in duplicate.

10.4 Blank Test

10.4.1 Separately pipette out 50 ml of the standard sodium oxalate solution into a 500 ml Erlenmeyer flask, add 50 ml of sulphuric acid and 200 ml water and immediately titrate with standard potassium permanganate keeping the temperature at 60° to 70°C till the last drop gives a persistent faint pink end point. This is the blank test volume (V_1).

10.5 Factor of the Standard Potassium Permanganate

10.5.1 Weigh duplicate test portions of a sample of standard certified manganese ore, having manganese dioxide content approximately the same as that of the sample, under analysis and pass them through all the stages of the analysis. The mass of the sample being same as that weighed for the sample under analysis.

10.5.2 Factor ' F ' of the standard potassium permanganate, expressed as grams of manganese dioxide corresponding to 1 ml of the solution, shall be calculated by the formula:

$$F = \frac{B \times M}{V \times 100}$$

where

B = manganese dioxide content, as percentage by mass of the standard sample of manganese ore;

M = mass, in grams, of the standard manganese ore sample; and

V = volume of potassium permanganate solution, in millilitres, consumed.

10.5.3 Calculate the mean of the factor ' F ', of the duplicate results rounded to six places of decimals.

10.6 Expression of Results

The manganese dioxide (MnO_2) in percent by mass is obtained by the following formula:

$$\text{MnO}_2 \text{ (percent)} = \frac{F (V_1 - V_2) \times 100 \times K}{m}$$

where

F = factor of the standard potassium permanganate solution;

V_1 = volume, in ml, of standard potassium permanganate solution in the blank test;

V_2 = volume, in ml, of standard potassium permanganate consumed in the test;

K = conversion factor of the manganese dioxide on dry basis (if the sample is directly taken for the test then $K = 1$); and

m = mass, in g, of the test sample.

10.7 Active Oxygen

Active oxygen may be calculated from MnO_2 , percent (m/m) as follows Active oxygen, percent (m/m) = MnO_2 , percent (m/m) $\times 0.184$ 0.

10.8 Permissible Tolerance Between Parallel Determinations

NOTE — It will be necessary to carry out inter-laboratory tests to determine the permissible tolerance between and within laboratories and include these values under this test.

11 DETERMINATION OF MANGANESE DIOXIDE BY FERROUS AMMONIUM SULPHATE METHOD

11.1 Outline of the Method

The sample is treated with known excess of standard ammonium iron (II) sulphate solution, in the sulphuric acid, to reduce the manganese dioxide present in the sample. The unreacted ferrous salt is titrated with standard potassium dichromate solution, in presence of sodium diphenylamine-sulphonate as indicator. The equivalent manganese dioxide is calculated from the volume of standard ferrous salt consumed. The method is generally applicable to the overall range of manganese ores/concentrates.

11.2 Reagents

11.2.1 *Phosphoric Acid*, sp. gr. 1.7.

11.2.2 *Standard Ferrous Ammonium Sulphate*, 60 g/l solution.

Dissolve 60 g ferrous ammonium sulphate $[(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}]$ in 50 ml sulphuric acid [1:7 (v/v)] and dilute to one litre with the same acid.

11.2.3 *Standard Potassium Dichromate*, 8.780 g/l [see IS 7659 (Part 1)]

11.2.3.1 *Standardization of potassium dichromate* — Take two test samples, weighed accurately to 0.25 g each, from a standard certified sample of manganese ore having a known manganese dioxide content, approximately the same as that of the sample to be analysed and treat them through all the stages of analysis detailed under 11.4.

The factor ' F ' of the potassium dichromate solution expressed as grams of manganese dioxide corresponding to 1 ml of the solution is calculated from the following formula:

$$F = \frac{B \times m}{V \times 100}$$

where

B = manganese dioxide content, percent (m/m) of standard certified manganese ore;

m = mass, in g, of the standard sample; and

v = volume, in millilitres, of potassium dichromate solution consumed by the standard sample.

Take the factor as the mean of the two results to six decimals.

11.2.4 *Sodium Diphenylamine-Sulphonate*, 0.8 g/l Solution — Dissolve 0.08 g of powdered sodium diphenylamine-sulphonate ($\text{C}_6\text{H}_5\text{NHC}_6\text{H}_4 \text{SO}_3\text{Na}$) in

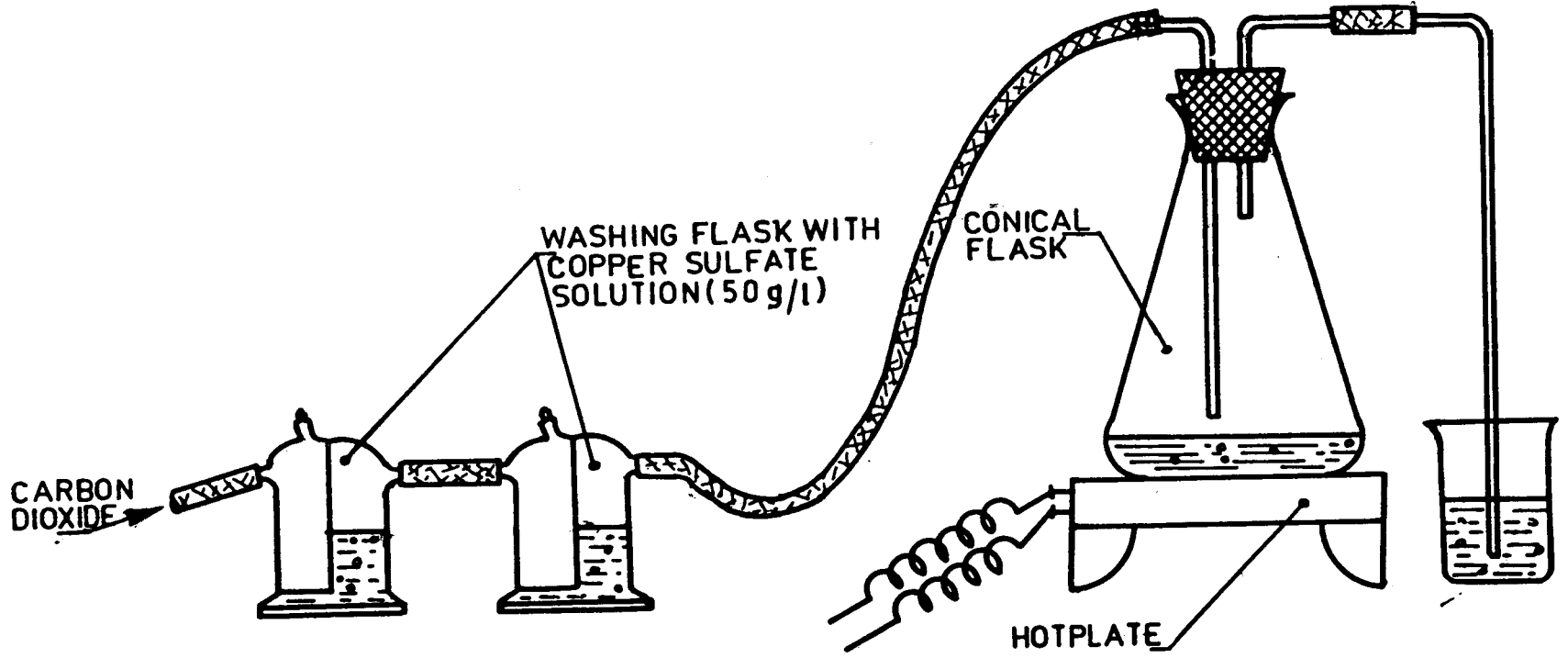


FIG. 1 EXAMPLE OF APPARATUS

a small volume of water and dilute with water to 100 ml. Store in a dark coloured bottle.

11.3 Apparatus

11.3.1 Conical flask, 300 ml, capacity fitted with a stopper with two outlet glass/tubes (see Fig. 1).

11.3.2 Source of Carbon Dioxide

11.3.3 Washing flasks, containing copper sulphate solution (50 g/l) (see Fig. 1), and set up of the system as shown in the Fig 1.

11.4 Procedure

11.4.1 The test sample shall preferably, be ground to pass 75 micron sieve.

11.4.2 The factor K , for the hygroscopic moisture, shall be determined, if required, on this test sample ground to 75 micron size.

11.4.3 The sample to be weighed for each test shall be 0.25 g. The test shall be performed in duplicate.

11.4.4 To the conical flask, containing accurately weighed test sample, add 50 ml of the ferrous ammonium sulphate solution and 50 ml sulphuric acid 1 : 9 (v/v). Close the flask with the stopper and allow a2 current of carbon dioxide to pass through it. Thoroughly mix and without stopping the current of carbon dioxide heat the contents of the flask moderately until the ore is dissolved (until the dark-coloured particles have disappeared) (see Fig 1).

11.4.5 Cool the contents of the flask (without stopping the current of carbon dioxide), then open the flask. Add 10 ml phosphoric acid and 2 ml of sodium diphenylamine-sulphonate indicator. Dilute with cold water (from which air has been removed by boiling) to 150 ml and titrate excess of ferrous ammonium sulphate with the standard potassium dichromate solution, until the solution becomes permanently violet-blue. Carry out the test in duplicate.

11.5 Blank Test

Separately transfer 50 ml of ferrous ammonium sulphate solution into 300 ml conical flask, add 50 ml sulphuric acid 1:9 (v/v) and 10 ml phosphoric acid, immediately titrate with standard potassium dichromate solution, until the solution becomes permanently violet-blue. Note the volume as V_1 ml.

11.6 Calculation

The manganese dioxide content (MnO_2) in percent by mass is obtained from the following formula:

$$\text{MnO}_2, \text{ percent} = \frac{F (V_1 - V_2) \times K \times 100}{m}$$

where

F = factor for standard potassium dichromate solution (11.2.3.1);

V_1 = volume, in ml, of standard potassium dichromate solution used in the blank test (11.5);

V_2 = volume, in ml, of standard potassium dichromate consumed in the determination;

m = mass, in g, of the test sample; and

K = conversion factor for expressing the MnO_2 , percent (m/m) content on dry basis. (If the dry test sample is directly used for the determination, then $K=1$.)

Calculate the mean MnO_2 , percent (m/m) from the duplicate tests, if they meet the permissible tolerance. If not, repeat the test.

11.7 Permissible Tolerance

The permissible tolerance of parallel determinations is given below:

MnO_2 (m/m)	Permissible Tolerance (m/m)
Up to 50	0.30
Above 50 up to 70	0.40
Above 70	0.50

12 DETERMINATION OF IRON BY THE DICHROMATE METHOD

12.1 Outline of the Method

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

This method is generally applicable to manganese ores having total iron content from 1 to 25 percent (m/m).

12.2 Reagents

12.2.1 Concentrated Ammonium Hydroxide, sp. gr. 0.90.

12.2.2 Ammonium Chloride Solution, 10 percent (m/v).

12.2.3 Dilute Hydrochloric Acid, 1 : 1 (v/v).

12.2.4 Stannous Chloride Solution—Dissolve by heating 60 g pure stannous chloride in 400 ml concentrated hydrochloric acid by constant stirring. Cool, add 600 ml of water and mix. Add a few pieces of granulated tin and preserve the solution in an air-tight amber coloured bottle.

12.2.5 Mercuric Chloride Solution — Prepare a saturated solution of mercuric chloride in water (approximately 50 g/l).

12.2.6 Concentrated Sulphuric Acid, sp. gr. 1.84 (see IS 266).

12.2.7 Syrupy Phosphoric Acid, 85 percent.

12.2.8 Sulphuric Phosphoric Acid Mixture — Add slowly 150 ml of concentrated sulphuric acid to 700 ml of water with constant stirring. Add to this 150 ml of syrupy phosphoric acid. Destroy any oxidizable impurities by adding potassium permanganate solution [0.3 percent (*m/v*)] dropwise, until the pink colour of potassium permanganate persists, and cool the solution.

12.2.9 Sodium Diphenylamine Sulphonate Indicator Solution — Dissolve 0.5 g of sodium diphenylamine-sulphonate in 100 ml water. Store in an amber-coloured bottle.

12.2.10 Potassium Dichromate, Standard Volumetric Solution

12.2.10.1 Solution A (0.1 N) — Dry pure potassium dichromate in an air oven at 105° to 110° C for 90 min, and cool in a desiccator. Weigh exactly 4.903 5 g of this potassium dichromate and transfer into a 500 ml beaker and dissolve in 200 ml water. Transfer the solution carefully to a 1 000 ml volumetric flask, using water at room temperature, dilute to the mark and mix well. Preserve this solution in an amber-coloured bottle.

1 ml of this solution, corresponds to 0.005 585 g of iron.

12.2.10.2 Solution B (0.05 N) — Weigh exactly 2.451 7 g of dried pure potassium dichromate (see 12.2.10.1) and transfer it into 500 ml beaker and dissolve in 200 ml water. Transfer the solution carefully to a 1 000 ml volumetric flask, dilute with water to the mark and mix well. Preserve in an amber-coloured bottle.

1 ml of this solution corresponds to 0.002 729 2 g of iron.

12.2.11 Standard Iron Solution : (5.58 g Fe/l) — Weigh 5.58 g metallic iron, of purity 99.9 percent (*m/m*) or more, into a 500 ml conical flask. Insert a small funnel into the neck of the flask. Add 110 ml of hydrochloric acid 1:2 (*v/v*) in small quantities at a time and heat, with funnel on, until iron is dissolved. Cool the solution and oxidize the iron with 5 ml of hydrogen peroxide [30 percent (*m/m*) solution] adding in small quantities. Heat to boiling and cool. Transfer to a 1 000 ml volumetric flask, dilute to the mark with water and mix.

1 ml of this standard solution corresponds to 1 ml of potassium dichromate standard solution A (see 12.2.10.1).

12.3 Procedure

Take aliquot from the main solution to represent 1 g of ore, containing 1 to 10 percent iron. For higher iron contents the aliquot shall represent 0.5 g of ore. Heat the solution to boil. Precipitate iron with concentrated ammonium hydroxide, in presence of 3 g ammonium chloride, till the smell of ammonia persists. Heat the solution to boiling and allow to stand for 10 min. After the precipitate has settled, filter the hot solution on a rapid filter paper and wash with hot water. Dissolve the precipitate on the filter with hot 10 ml hydrochloric acid, using small portions, in a beaker. Wash with hot hydrochloric acid till all precipitate dissolves and wash with hot water. Reprecipitate the iron as hydroxide with ammonium hydroxide solution following the procedure given above and filter hot, on a rapid filter paper. Wash with hot water till free from ammonia. Preserve the combined filtrates for the determination of calcium and magnesium.

Dissolve the precipitate in hot dilute hydrochloric acid, and collect the filtrate and washings in 250 ml beaker. Heat to boiling and to the boiling solution, add stannous chloride drop by drop with continuous stirring until the solution just becomes colourless. Add two to three drops of stannous chloride solution in excess, and cool to room temperature. Add about 10 ml of mercuric chloride solution and shake. At this stage a silky white precipitate appears. If it fails to appear or if a blackish precipitate appears, repeat the test. Allow to stand for about 2 to 5 min.

Add 15 ml of sulphuric-phosphoric acid mixture and transfer to a 500 ml beaker quantitatively. Dilute to 400 ml. Add three to four drops of sodium diphenylamine sulphonate indicator and titrate it slowly while constantly stirring with standard potassium dichromate solution, until the green colour begins to darken. Continue titration slowly till a drop of the dichromate solution gives a permanent violet-blue colouration.

NOTE — For ores containing less than 5 percent (*m/m*) of total iron, use potassium dichromate standard solution B for titration, for ores containing more than 5 percent (*m/m*) of total iron, use potassium dichromate standard solution A for titration.

12.4 Blank Test

Parallel with the chemical analysis of the sample, use 1.00 ml of standard iron solution, instead of the sample, for the blank test, using same quantities of the reagents, used in the procedure. Titrate with standard potassium dichromate solution A or B. Subtract the amount of the

standard potassium dichromate solution A or B corresponding to 1.00 ml of the standard iron solution from the titrated volume and take it as the blank test value.

12.4.1 Standardization of Standard Potassium Dichromate Solution A or B

The factor 'F' of the standard potassium dichromate solution A or B shall be determined against duplicate portions of a standard certified sample of Manganese Ore, having approximately the same iron content as that of the sample to be analyzed, passing them through all the stages of the analysis.

The factor 'F' expressed as gram of iron corresponding to 1.00 ml of the standard potassium dichromate solution is given by:

$$F = \frac{B \times M}{V \times 100}$$

where

B = Fe, percent (m/m) of the standard manganese ore;

M = mass in g of the standard manganese ore sample taken for analysis; and

V = volume, in ml, of the standard potassium dichromate solution used in the titration.

Take the factor F , as the mean of the two results, correct to six places of decimal.

12.5 Calculation

The total iron content, expressed as percentage by mass is given by:

$$\text{Iron, percent} = \frac{F (V_1 - V_2) \times 100 \times K}{m}$$

where

F = factor of the standard potassium dichromate solution A or B expressed, in grams of iron per millilitre;

V_1 = volume, in ml, of standard potassium dichromate solution A or B, consumed during titration of the test sample;

V_2 = volume, in ml, of standard potassium dichromate solution A or B, consumed during titration of the blank solution (deducting the volume of standard potassium dichromate solution A or B corresponding to 1.00 millilitre of standard iron solution);

m = mass, in g, of the test sample; and

K = conversion factor for the expression of the total iron content, on the dry basis. K will be

equal to 1, if dried sample is directly used for the analysis.

Calculate the mean iron, percent (m/m) of the duplicate tests if they meet permissible tolerance.

12.6 Permissible Tolerance on Results of Parallel Determination

Total Iron Content, percent (m/m)	Permissible Tolerance of Two Parallel Determinations, percent (m/m)
From 1.0 up to 5.0	0.12
Above 5.0 up to 10.0	0.20
Above 10.0 up to 25.0	0.30
Above 25.0 up to 40.0	0.45

NOTE — In case the iron content of manganiferrous iron ore is required to be determined by using this standard procedure, then the permissible tolerance indicated will be applicable.

13 DETERMINATION OF ALUMINA BY THE OXINE METHOD

13.1 Outline of the Method

Iron and manganese are precipitated by passing hydrogen sulphide in the ammoniacal solution of the sample in presence of tartaric acid which keeps alumina and titania in solution. After boiling off hydrogen sulphide from the solution, aluminium is precipitated in the acetate medium and weighed as oxinate. Necessary correction for titanium is made.

13.2 Reagents

13.2.1 Concentrated Hydrochloric Acid, see 6.2.1.

13.2.2 Tartaric Acid, solid.

13.2.3 Concentrated Ammonium Hydroxide, sp. gr. 0.90.

13.2.4 Hydrogen Sulphide, gas.

13.2.5 Ammonium Sulphide Solution — Prepare a weak solution of ammonium sulphide containing one percent sodium potassium tartrate.

13.2.6 Methyl Red Indicator Solution — Dissolve 0.1 g of methyl red in 100 ml of rectified spirit (see IS 323).

13.2.7 Oxine (8-Hydroxyquinoline) Solution — Dissolve 5g of 8-hydroxyquinoline in 10 ml of glacial acetic acid and dilute to 100 ml with water.

13.2.8 Ammonium Acetate, solid.

13.3 Procedure

13.3.1 Take an aliquot from the solution reserved under 7.3 representing 0.1 to 0.5 g of the sample. Add

2 to 3 g of tartaric acid, make strongly ammoniacal with concentrated ammonium hydroxide and pass hydrogen sulphide gas for 10 to 15 min.

13.3.2 Filter and wash the precipitate with weak ammonium precipitate, acidify the filtrate with concentrated hydrochloric acid and boil the solution until all hydrogen sulphide is expelled. Filter the precipitated sulphur, wash with hot water and concentrate the filtrate to 100 ml. Make the solution just acidic with concentrated hydrochloric acid using methyl red as indicator.

13.3.3 Dilute to 200 ml and adjust the temperature of the solution to about 70° C. Add 25 ml of oxine solution followed by 7 to 8 g of ammonium acetate, added with stirring. Maintain the solution at 70° to 80°C until the precipitate has settled down. Allow to stand for 1 to 2 h filter and wash the precipitate with hot water 10 to 12 times. Dry the precipitate at 110 to 120°C and weigh as oxinate.

13.3.4 Titanium will also be precipitated along with aluminium as oxinate. Apply the correction as given under 13.4.

13.4 Calculation

$$\text{Alumina, percent} = \frac{(A - B) \times 0.111 \times 100}{C}$$

where

A = weight, in g, of the impure oxinate as precipitated under 13.3.3;

B = weight, in g, of the titanium oxinate as calculated below:

$\text{TiO}(\text{C}_5\text{H}_6\text{ON})_2 = \text{Ti} \times 7.346$ (Titanium, in grams, in sample); and

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

14 DETERMINATION OF PHOSPHORUS BY THE ALKALIMETRIC METHOD

14.1 Outline of the Method

The sample is dissolved in hydrochloric acid and evaporated to dryness. The dry mass, after the removal of arsenic, is taken up in nitric acid and filtered. Phosphorus left in the residue is recovered and is precipitated from the combined filtrate as ammonium phosphomolybdate, which, after washing, is dissolved in known excess of standard alkali. The unreacted alkali is backtitrated with standard sulphuric acid. The range of phosphorous applicable to this shall be > 0.015 percent (*m/m*).

14.2 Reagents

14.2.1 Concentrated Hydrochloric Acid, see 6.2.1.

14.2.2 Ammonium Bromide, solid.

14.2.3 Concentrated Nitric Acid, see 8.2.2.

14.2.4 Sodium Carbonate, anhydrous.

14.2.5 Dilute Hydrochloric Acid, 1:1 (v/v).

14.2.6 Concentrated Ammonium Hydroxide, sp. gr. 0.90.

14.2.7 Ammonium Nitrate, solid.

14.2.8 Ammonium Molybdate Solution — Add solution A (see 14.2.8.1) slowly and with constant stirring to solution B (see 14.2.8.2) kept cool in a cold water bath. Add 10 ml of ammonium phosphate solution (one gram per litre) and keep the solution at least for 24 h. Filter the solution before use.

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

14.2.8.2 Solution B — Add 490 ml of concentrated nitric acid to 1 150 ml of water and cool.

14.2.9 Dilute Nitric Acid, 2:98 (v/v).

14.2.10 Potassium Nitrate Wash Solution, one percent (v/v).

14.2.11 Sodium Hydroxide Solution, 0.1 N.

14.2.12 Phenolphthalein Indicator Solution — Dissolve 0.5 g of the reagent in 100 ml of alcohol (60 percent).

14.2.13 Standard Sulphuric Acid — 0.1 N. Dilute 2.5 to 3 ml of concentrated sulphuric acid to one litre and standardize against sodium carbonate.

14.2.13.1 Standardization of sulphuric acid, 0.1 N— Pipette out an aliquot of standard sodium carbonate solution (0.1 N) and titrate against standard sulphuric acid using 6 drops of methyl orange [0.1 percent (*m/m*)] till the colour of the solution becomes slightly red.

$$\text{Normality of sulphuric acid} = \frac{V_1 \times 0.1}{V_2}$$

where

V_1 = volume, in ml, of sodium carbonate (0.1 N) solution; and

V_2 = volume, in ml, of sulphuric acid consumed during titration.

14.3 Procedure

14.3.1 Transfer about 3 g of the accurately weighed test sample into a conical flask and digest with 30 to 35 ml of concentrated hydrochloric acid on a hot-plate. Evaporate the solution to dryness. Add 5 ml of concentrated hydrochloric acid and about 1 g of ammonium bromide and again evaporate until dry, to remove arsenic. Add 10 ml of concentrated nitric acid to the dry mass and filter the solution. Preserve the filtrate.

14.3.2 Fuse the residue with 8 to 10 times of its weight of sodium carbonate. Lixivate the fused mass with 50 to 60 ml of dilute hydrochloric acid. Evaporate to dryness and bake at about 100°C. Add 5 to 10 ml of concentrated hydrochloric acid, boil and dilute to about 50 ml, filter and wash the residue. Mix the filtrate with that preserved under 14.3.1.

14.3.3 Evaporate the combined filtrate to about 100 ml and neutralize with concentrated ammonium hydroxide until a slight persistent precipitate forms. Dissolve the precipitate in few drops of concentrated nitric acid, add 1 to 2 ml in excess and heat to about 80°C. Add 10 to 15 g of ammonium nitrate and 40 ml of ammonium molybdate solution with vigorous stirring. Continue stirring till the phosphorus is precipitated. Keep at 50° to 60°C for an hour.

14.3.4 Filter the precipitate through a thick pad of filter paper pulp prepared on a perforated disc in a funnel. Wash the precipitate with dilute nitric acid four to five times and then with potassium nitrate, wash solution till 10 ml of the filtrate collected in a test tube do not consume more than one drop of 0.1 N sodium hydroxide solution using a drop of phenolphthalein indicator solution (begin testing the filtrate from third wash). Transfer the pad with the precipitate back to the beaker in which phosphorus was precipitated. Add 25 ml of water and add an excess of sodium hydroxide solution with stirring until all the yellow precipitate has dissolved and the solution is colourless. Add few millilitres of standard sodium hydroxide solution in excess and titrate with standard sulphuric acid using phenolphthalein indicator solution.

14.3.5 Carry out a blank using the same quantity of sodium hydroxide solution as was added in the test and titrate with standard sulphuric acid. The test shall be carried out in duplicate.

14.4 Calculation

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

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;

D = weight, in g, of the sample taken; and

K = for the expression of phosphorous on dry basis. If the dried test sample is taken directly for the test, then $K = 1$.

Mean of the phosphorous percent (m/m) of the duplicate tests, shall be reported, if they meet the permissible tolerance, if not, then repeat the test.

14.5 Permissible Tolerance

The permissible tolerance values shall be added later after conducting inter-laboratory tests.

15 DETERMINATION OF SULPHUR BY THE GRAVIMETRIC METHOD

15.1 Outline of the Method

After repeated evaporation of the sample with aqua-regia and hydrochloric acid, the dry mass is taken up with water and filtered. The ignited residue is hydro-fluorized, fused with sodium carbonate and extracted with water. Iron in the extract is reduced and sulphate precipitated as barium sulphate in acid medium. This method is applicable for manganese ores containing sulphur in the range of 0.01 to 0.20 percent (m/m).

15.2 Reagents

15.2.1 Concentrated Hydrochloric Acid, see 6.2.1.

15.2.2 Concentrated Nitric Acid, see 8.2.2.

15.2.3 Aqua Regia — Mix concentrated hydrochloric acid and concentrated nitric acid in the ratio of 3:1.

15.2.4 Dilute Hydrochloric Acid, 1:99 (v/v).

15.2.5 Hydrofluoric Acid, 40 percent.

15.2.6 Sodium Carbonate, anhydrous.

15.2.7 Sodium Carbonate Solution, one percent (w/v).

15.2.8 Concentrated Ammonium Hydroxide, sp. gr. 0.90.

15.2.9 Zinc, granulated.

15.2.10 Barium Chloride Solution, 20 percent (w/v). Dissolve 20 g of barium chloride crystals ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) in water and dilute to 100 ml.

15.3 Procedure

15.3.1 Weigh accurately about 5 g of the test sample in a 400 ml beaker, and add 60 ml of aqua-regia. After the ore has been attacked, evaporate the solution to

dryness. Cool, add 25 ml of concentrated hydrochloric acid and again evaporate to dryness. Cool the residue, add 25 ml of concentrated hydrochloric acid and 50 ml of hot water. Boil for few minutes and filter hot. Wash the residue six times with hot dilute hydrochloric acid and then with hot water. Preserve the solution.

15.3.2 Transfer the residue with the filter to a platinum crucible and ignite at 500° to 600°C. Moisten the ignited residue with 10 to 12 drops of concentrated nitric acid and add 15 ml of hydrofluoric acid, evaporate to dryness and ignite at about 400°C. Fuse the residue in the crucible with three to four grams of sodium carbonate at about 1 000°C. Lixivate the fused mass with 50 ml of hot water and filter. Wash the residue eight to ten times with sodium carbonate solution. Mix the filtrate with the solution preserved under 15.3.1.

15.3.3 Neutralize the combined solution obtained under 15.3.2 with concentrated ammonium hydroxide until a faint persistent precipitate forms. Dissolve the precipitate in the minimum amount of concentrated hydrochloric acid and add 7 to 8 ml in excess. Reduce the iron in the solution with two to three grams of granulated zinc, and warm on a steam bath. Filter and wash with hot dilute hydrochloric acid three to four times. Concentrate the solution and adjust the acidity so that the solution contains two percent by volume of hydrochloric acid. Heat the solution to boiling and add 20 ml of warm barium chloride solution dropwise with constant stirring. Let the solution stand for 2 h at steam-bath overnight at the room temperature. Filter the precipitate and wash it with cold dilute hydrochloric acid and then with hot water until free from chlorides. Dry and ignite the precipitate in a weighed platinum or porcelain crucible and weigh as barium sulphate.

The test shall be performed in duplicate.

15.3.4 Permissible Tolerance Between Duplicate Determination

The permissible tolerance between parallel determinations of sulphur content, shall be added after conducting the tests.

15.4 Calculation

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

where

A = weight, in g, of barium sulphate;

B = weight, in g, of the sample taken; and

K = for the expression of sulphur content on dry basis (If the dried test sample is directly taken for the test, then *K* = 1).

16 ATOMIC ABSORPTION METHOD

16.1 A.A.S. Instrument Parameters

16.1.1 Silicon (Si)	
Wavelength	251.6 nm
Background correction	On
Spectral Bandpass	0.2 mA
Lamp current	20 mA
Fuel & support	Acetylene-nitrous oxide
Flame stoichiometry	Strongly reducing yellow outer edge, red cone 2-3 cm high
16.1.2 Aluminium (Al)	
Wavelength	309.3 nm
Spectral bandpass	0.5 nm
Background correction	Off
Lamp current	10 mA
Fuel & support	Acetylene-Nitrous oxide
Flame stoichiometry	Reducing red cone 1-2 cm high
16.1.3 Titanium (Ti)	
Wavelength	364.3 nm
Spectral bandpass	0.5 nm
Lamp current	20 mA
Background correction	Off
Fuel & support	Acetylene-Nitrous oxide
Flame stoichiometry	Reducing red cone 1-1.5 cm
16.1.4 Calcium (Ca)	
Wavelength	422.7 nm
Spectral bandpass	0.5 nm
Lamp current	3.5 mA
Background correction	Off
Fuel & support	Acetylene-Nitrous oxide
Flame stoichiometry	Reducing red cone 1-1.5 cm
16.1.5 Magnesium (Mg)	
Wavelength	285.2 nm
Spectral bandpass	0.5 nm
Lamp current	3.5A
Background correction	On
Fuel & support	Acetylene-Nitrous oxide
16.1.6 Manganese (Mn)	
Wavelength	403.1
Spectral bandpass	0.2 nm
Lamp current	5 mA

Background correction	Off	Lamp current	7 mA
Fuel & support	Acetylene-Nitrous oxide	Background correction	On
		Fuel & support	Acetylene-air
		Flame stoichiometry	Oxidising
16.1.7 Iron (Fe)		16.1.14 Chromium (Cr)	
Wavelength	422.7 nm	Wavelength	357.9 nm
Spectral bandpass	0.5 nm	Spectral bandpass	0.2 nm
Lamp current	3.5 mA	Lamp current	7 mA
Background correction	Off	Background correction	Off
Fuel & support	Acetylene-Nitrous oxide	Fuel & support	Acetylene-air
Flame stoichiometry	Reducing red cone 1-1.5 cm	Flame stoichiometry	Reducing
16.1.8 Sodium (Na)		16.1.15 Vanadium (V)	
Wavelength	589.0 nm	Wavelength	318.5 nm
Spectral bandpass	0.5 nm	Spectral bandpass	0.2 nm
Lamp current	5 mA	Lamp current	20 mA
Background correction	Off	Background correction	Off
Fuel & support	Acetylene-air	Fuel & support	Acetylene-Nitrous oxide
Flame stoichiometry	Oxidising	Flame stoichiometry	Red cone 1-1.5 cm
16.1.9 Potassium (K)		17 PRINCIPLE : DECOMPOSITION PROCEDURE	
Wavelength	766.5 nm	The sample is decomposed by acid digestion. Initially sample is attacked by concentrated hydrochloric acid followed by overnight cold digestion by HF. The excess of fluoride is then complexed with boric acid. For calibrating the instrument, the standard used should, preferably, be an International Standard reference Manganese Ore of known value. The standard reference Manganese Ore of known value selected must be digested in the same way as any unknown sample, then aspirate on the AAS along with the sample for the determination of SiO ₂ , Al ₂ O ₃ , TiO ₂ , Na ₂ O, K ₂ O, CaO, MgO and Fe ₂ O ₃ .	
Spectral bandpass	1.0 nm		
Lamp current	5 mA		
Background correction	Off		
Fuel & support	Acetylene-air		
Flame stoichiometry	Reducing, slightly luminous		
16.1.10 Copper (Cu)			
Wavelength	324.7 nm		
Spectral bandpass	0.5 nm		
Lamp current	3.5 mA		
Background correction	Off		
Fuel & support	Acetylene-air		
Flame stoichiometry	Oxidising		
16.1.11 Lead (Pb)		18 REAGENTS AND STANDARDS	
Wavelength	217.0 nm	All chemicals should be of recognized analyzed reagent grade. Demineralised water of high purity should be used.	
Spectral bandpass	1.0 nm		
Lamp current	10 mA		
Background correction	On		
Fuel and support	Acetylene-air		
Flame Stoichiometry	Oxidising		
16.1.12 Zinc (Zn)		18.1 Standard Silica Solution (1 000 µg/ml SiO₂)	
Wavelength	213.9 nm	Fuse 0.1 g powdered quartz with about 2.5 g of anhydrous sodium carbonate in a platinum crucible. Cool, dissolve the mass in warm water and dilute to 100 ml in a volumetric flask. Store in a polythene bottle.	
Spectral bandpass	1.0 nm		
Lamp current	5 mA		
Background correction	On		
Fuel & support	Acetylene-air		
Fame stoichiometry	Oxidising		
16.1.13 Cobalt (Co)		18.2 Standard Aluminium Solution (1 000 µg/ml Al₂O₃)	
Wavelength	240.7 nm	Dissolve 0.264 6 g of metallic aluminium (aluminium foil or wire, 99.99 percent purity) in 20 ml of aqua regia. Evaporate on water bath near dryness. Make up with 20 ml HCl (1:1), transfer to a 500 ml capacity volumetric flask and make up with 2 N HCl.	
Spectral bandpass	0.2 nm		

NOTE — In the event of non-availability of standard reference material, standard addition method is to be used.

18.3 Standard Titanium Solution (1 000 µg/ml TiO₂)

Fuse 0.1 g titanium dioxide (ignited) with about 0.5 g of potassium pyrosulphate in a silica crucible. Cool, dissolve the melt in dilute sulphuric acid (1:10) and dilute to 100 ml in a volumetric flask.

18.4 Standard Iron Solution (1 000 µg/ml Fe₂O₃)

Dissolve 0.349 7 g of metallic iron (iron wire 99.9 percent purity) in 20 ml aqua regia. Evaporate in water bath to near dryness, make up with 20 ml HCl (1:1), transfer to a 500 ml capacity volumetric flask and make up with 2N HCl.

18.5 Standard Manganese Solution (1 000 µg/ml MnO)

Dissolve 0.387 2 g of metallic manganese (coarse powder, 99.99 percent purity) in 20 ml HCl. Transfer to a 500 ml capacity volumetric flask and make up volume with 2 N HCl.

18.6 Standard Calcium Solution (100 µg/ml CaO)

Dissolve 0.892 4 g of calcium carbonate (dried at 110°C) in 50 ml HCl(1:1), transfer to a 500 ml capacity volumetric flask and make up volume with 2 N HCl. This is 1 000 µg/ml CaO solution.

18.7 Standard Magnesium Solution (100 µg/ml MgO)

Dissolve 0.301 5 g of metallic magnesium (magnesium foil or wire, 99.99 percent purity) in 50 ml HCl (1:1), transfer to a 500 ml capacity volumetric flask and make up volume with 2 N HCl. This is 1 000 µg/ml MgO solution.

18.8 Standard Copper Solution (1 000 µg/ml Cu)

Dissolve 1.000 g of copper metal (copper metal strip or wire, 99.99 percent purity) in a minimum volume of 1:1 nitric acid and dilute to one litre with 2 N HNO₃ in a volumetric flask.

18.9 Standard Lead Solution (1 000 µg/ml Pb)

Dissolve 1.000 g lead metal (lead metal strip or wire, 99.99 percent purity) in minimum volume of 1:1 nitric acid. Dilute to one litre with 2 N HNO₃ in a volumetric flask.

18.10 Standard Zinc Solution (1 000 µg/ml Zn)

Dissolve 1.000 g zinc metal (Zinc granules, 99.99 percent purity) in 40 ml of 1:1 HCl and dilute to 1 litre with 2 N HCl in a volumetric flask.

18.11 Standard Cobalt Solution (1 000 µg/ml Co)

Dissolve 1.000 g of cobalt metal (cobalt metal strip or wire of 99.99% purity) in minimum volume of 1:1

nitric acid and dilute to one litre with 2 N HCl in a volumetric flask.

18.12 Standard Chromium Solution (1 000 µg/ml Cr)

Dissolve 1.000 g of chromium metal (chromium metal strip or wire of 99.99 percent purity) in minimum volume of HCl with gentle heating. Cool and dilute to one litre with 2 N HCl in a volumetric flask.

18.13 Standard Vanadium Solution (1 000 µg/ml V)

Dissolve 1.000 g of vanadium metal (vanadium metal granules of 99.99 percent purity) in 40 ml of nitric acid and dilute to one litre with 2 NHNO₃ in a volumetric flask.

18.14 Standard Sodium Solution (1 000 µg/ml Na₂O)

Dissolve 1.710 1 g of sodium carbonate, 99.99 percent purity (dried at 110°C) in minimum amount of 1:1 HCl taking care of effervescence by closing with a watch glass and dilute to one litre with 2 N HCl in a volumetric flask.

18.15 Standard Potassium Solution (1 000 µg/ml K₂O)

Dissolve 1.583 8 g of dried potassium chloride AR Gr. in water and dilute one litre with 2 N HCl in a volumetric flask.

18.16 Mix calibration solution for silica, aluminum, titanium (Range 5, 20 40, 80, 100 mg/ml SiO₂, Al₂O₃, TiO₃); calcium, magnesium, sodium, potassium, chromium (Range 0.25, 0.5, 1.0, 1.5, 2.0 mg/ml of CaO, MgO, Na₂O, K₂O, Cr, Fe₂O₃ (Range 5, 10, 20, 25, 30 mg/ml) and blank solution.

Take appropriate aliquots of standard silica solution (*see* 18.1), standard aluminium solution (*see* 18.2), standard titanium solution (*see* 18.2), standard calcium solution (*see* 18.3), standard potassium solution (*see* 18.5), standard chromium solution (*see* 18.12) and standard iron solution (*see* 18.4) in a series of polythene volumetric flasks of required volume. Add 5 ml of 1 000 mg/ml Mn (*see* 18.5) and make up the volume with standard boric acid solution in 2 N HCl (*see* 18.18), Prepare blank by taking 5 ml of 100 mg/ml Mn (*see* 18.18) in the same capacity volumetric flask as prepared for the standards and make up with standard boric acid solution in 2 N HCl (*see* 18.18).

18.17 Mixed Calibration Solution For Cu, Pb, Zn, Co (Range 0.5, 1.0, 2, 4 mg/ml) V Solution (Range 10, 20, 40, 60 mg/ml) and Blank Solution.

Take appropriate aliquots of standard Cu solution (*see* 18.8), standard Pb solution (*see* 18.9), standard

Zn solution (*see* 18.10), standard cobalt solution (*see* 18.11), and standard vanadium solution (*see* 18.13) in a series of polythene volumetric flasks of required volume. Add 5 ml of 1 000 µg/ml Mn (*see* 18.5) and make up the volume with 2 N HCl. Prepare blank by taking 5 ml of 1 000 µg/ml Mn (*see* 18.5) in the same capacity volumetric flask as prepared for standard and make up with 2 N HCl.

18.18 Standard Boric Acid Solution 2N HCl

Prepare sufficient amount of supersaturated boric acid solution of 2 N HCl.

19 PROCEDURE

The sample should be properly dried and powdered to -200 mesh size. The analysis should be carried out preferably in duplicate in each sample.

19.1 Weigh exactly 0.2 g of the sample in a teflon beaker, add 10 ml of concentrated HCl, cover with Teflon lid, heat over a water bath till all the black particles disappear. Cool, then add 1 to 2 ml of hydrofluoric acid, swirl occasionally and leave overnight. Similarly process the international standard Manganese ore or Manganese ore of known values by weighing 0.05 g, 0.10 g, 0.15 g and 0.20 g. Next day make up these test solutions and standard solutions in 50 ml polythene volumetric flasks with standard boric acid solution in HCl (*see* 18.18). This test solution may be used for the determination of SiO₂, Al₂O₃, TiO₂, Na₂O, K₂O, CaO, MgO and Fe₂O₃ by making appropriate dilutions as required for the estimation.

19.2 For trace element analysis weigh 0.2 g of the

sample in dry graduated test tube, digest with 5 ml of concentrated HCl for 5 h over a hot plate. Cool, make up to 20 ml with water. Weigh 0.05 g, 0.10 g, 0.10 g, 0.15 g and 0.20 g of International Standard Manganese ore or manganese ore of known values in dry graduated test tubes and process the same way as samples. This test solution may be used for the determination of Cu, Pb, Zn, Co and V.

19.3 Atomic Absorption Measurements

19.3.1 Set the atomic absorption instrument parameters as mentioned in our procedure or as recommended by the manufacturers. It may be required to rotate the burner head through 90°C (perpendicular to the light beam) for measurement of manganese and magnesium.

19.3.2 Calculation

The analyte concentration expressed as percentage of metal oxide or element is calculated from the following formula:

$$X = \frac{m \times 100}{M}$$

where

X = stands for the weight percentage of the oxide or element, that is, SiO₂, Al₂O₃, TiO₂, Fe₂O₃, MgO, CaO, Na₂O, K₂O or elements Cu, Pb, Zn, Co, Cr, V;

m = microgram of oxide per millilitre of test solution; and

M = mass, in microgram per millilitre, of sample in the test solution.

ANNEX A

(Clause 5.5)

TEST ANALYSIS

The results of chemical analysis may be reported in the following format:

- a) Name of the laboratory and its address,
- b) Sample reference number,
- c) Date of reporting,
- d) Identification of the sample in detail,
- e) Method of analysis, and
- f) Any other remarks, deemed necessary.

Moisture (on sample dried at $105 \pm 5^\circ\text{C}$) percent

CHEMICAL ANALYSIS ON SAMPLE DRIED AT $105 \pm 5^\circ\text{C}$

		<i>Percent</i>			<i>Percent</i>
Manganese dioxide	(MnO ₂)	Available oxygen	(O ₂)
Manganous oxide	(MnO)	Combined water	(C.W.)
Ferric oxide	(Fe ₂ O ₃)	Loss on ignition	(LOI)
Silica	(SiO ₂)	Copper	(Cu)
Alumina	(Al ₂ O ₃)	Arsenic	(As)
Barium oxide	(BaO)	Lead	(Pb)
Calcium oxide	(CaO)	Chromium	(Cr)
Magnesium oxide	(MgO)	Nickel	(Ni)
Sodium oxide	(Na ₂ O)	Cobalt	(Co)
Potassium oxide	(K ₂ O)	Total Manganese	(Mn)
Titania	(TiO ₂)	Iron	(Fe)
Phosphorous pentoxide	(P ₂ O ₅)	Phosphorous	(P)
Sulphur trioxide	(SO ₃)	Sulphur	N

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