

इंटरनेट

मानक

Disclosure to Promote the Right To Information

Whereas the Parliament of India has set out to provide a practical regime of right to information for citizens to secure access to information under the control of public authorities, in order to promote transparency and accountability in the working of every public authority, and whereas the attached publication of the Bureau of Indian Standards is of particular interest to the public, particularly disadvantaged communities and those engaged in the pursuit of education and knowledge, the attached public safety standard is made available to promote the timely dissemination of this information in an accurate manner to the public.

“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 1760-3 (1992): Methods of chemical analysis of limestone, dolomite and allied materials, Part 3: Determination of iron oxide, alumina, calcium oxide and magnesia [MTD 13: Ores and Raw Materials]



“ज्ञान से एक नये भारत का निर्माण”

Satyanarayan Gangaram Pitroda

“Invent a New India Using Knowledge”



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

Bhartḥari—Nitiśatakam

“Knowledge is such a treasure which cannot be stolen”

BLANK PAGE



भारतीय मानक

चूना, पत्थर, डोलोमाइट एवं सम्बद्ध सामग्री का
रासायनिक विश्लेषण

भाग 3 लोह, आक्साइड, ऐलुमिना, कैल्शियम आक्साइड एवं मैग्नीशिया ज्ञात करना
(पहला पुनरीक्षण)

Indian Standard

CHEMICAL ANALYSIS OF LIMESTONE,
DOLOMITE AND ALLIED MATERIALS

PART 3 DETERMINATION OF IRON OXIDE, ALUMINA,
CALCIUM OXIDE AND MAGNESIA

(*First Revision*)

First Reprint SEPTEMBER 1996

UDC 553.551 : 543 [546.72-3]

© BIS 1992

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

FOREWORD

This Indian Standard (Part 3) (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.

IS 1760 was first published in 1962. It covers the determination of different elements in various grades of minerals like limestone, dolomite, calcite and magnesite. It also covers the methods for magnesite refractories. The committee decided to revise this standard into different parts covering determination of each element in a separate part, which on publication would supersede the determination of that element given in IS 1760 : 1962. This Part covers determination of iron oxide, alumina, calcium oxide and magnesia. Other parts in the series are as follows:

- Part 1 Determination of loss on ignition
- Part 2 Determination of silica
- Part 3 Determination of carbon dioxide
- Part 4 Determination of chlorides

In this part the following changes have been made:

- a) The determination of ferric oxide by colorimetric method (for iron content ≤ 0.5 percent) and the permanganate method (for iron content ≥ 0.5 percent) has been replaced by spectrophotometric method.
- b) The determination of alumina by 'oxine method' has been replaced by 'EDTA method'.
- c) The determination of calcium oxide by 'the oxalate method' (applicable to minerals other than magnesite) and by 'the pyrophosphate method' (applicable to dolomite and limestone) has been replaced by 'EDTA method'.
- d) The determination of magnesium oxide in magnesite by 'the phosphate method' and determination of magnesium oxide in calcite by 'the oxine method' have been replaced by EDTA method.

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***CHEMICAL ANALYSIS OF LIMESTONE,
DOLOMITE AND ALLIED MATERIALS****PART 3 DETERMINATION OF IRON OXIDE, ALUMINA,
CALCIUM OXIDE AND MAGNESIA***(First Revision)***1 SCOPE**

1.1 This standard (Part 3) describes methods for chemical analysis of various grades of limestone, dolomite, calcite, and magnesite, in the ranges given below:

<i>Element</i>	<i>Range</i> (<i>Percent by Mass</i>)
Iron oxide (Fe_2O_3)	0.2 to 2
Alumina (Al_2O_3)	0.2 to 2
Calcium oxide (CaO)	0.5 to 55
Magnesium oxide (MgO)	0.2 to 52

2 REFERENCES

The following Indian Standards are necessary adjuncts to this standard:

<i>IS No.</i>	<i>Title</i>
264 : 1976	Nitric Acid (<i>second revision</i>)
1070 : 1977	Water for general laboratory use (<i>second revision</i>)
2109 : 1982	Methods of sampling of dolomite, limestone and other allied materials

3 SAMPLING

3.1 The sample shall be drawn and prepared in accordance with IS 2109 : 1982.

3.2 Grind 5 to 10 g of the laboratory sample so that it passes through IS Sieve 15 (100 mesh). Dry to constant mass at $105 \pm 2^\circ\text{C}$ and use it for the purpose of chemical analysis.

4 QUALITY OF REAGENTS

Unless specified otherwise, analytical grade reagents and distilled water (*see* IS 1070 : 1977) shall be employed for the test.

5 PREPARATION OF MAIN SOLUTION**5.1 Reagents**

5.1.1 *Dilute Hydrochloric Acid*, 1 percent, 40 percent (*v/v*).

5.1.2 Fusion Mixture

Mix carbonates of sodium and potassium in equal proportion.

5.1.3 *Dilute Sulphuric Acid*, 1 : 4 and 1 : 1 (*v/v*).

5.1.4 *Hydrofluoric Acid*, 40 percent (*v/v*).

5.2 Procedure**5.2.1 For Other than Magnesite Refractory Materials**

5.2.1.1 Weigh accurately 2.5 g of the test sample into a beaker or a porcelain dish and add to it 40 to 50 ml of dilute hydrochloric acid, covering the beaker by means of a suitable cover glass immediately after addition of the acid. As soon as effervescence stops, wash the lower surface of the cover glass into the beaker and set the contents for drying and baking at 110° to 115°C . After baking for about 20 to 25 minutes, cool to room temperature, add 25 to 30 ml dilute hydrochloric acid (40 percent) boil and filter. Transfer thoroughly the residue in the beaker as well as that adhering to the sides of the beaker to the filter, by hot water. Wash with hot dilute hydrochloric acid (1 percent) and then with hot water. Wash the filter free from chlorides by means of hot water. Collect the filtrate and washings in the same beaker and preserve it (A).

5.2.1.2 Transfer the filter paper with its residue into a previously heated platinum crucible and char at low temperature. Finally ignite at 900° to 950°C and cool.

5.2.1.3 Fuse the residue in the platinum crucible with about 3 g of fusion mixture. Cool and extract the melt in about 50 ml of dilute hydrochloric acid (40 percent). Mix with the filtrate from 5.2.1.1 and repeat the process of drying and baking. Extract the baked mass with about 30 to 40 ml of dilute hydrochloric acid and filter. Transfer all the silica in the beaker to the filter thoroughly by means of hot water. Wash silica on the filter free from chlorides by means of hot water. Collect the filtrate and washings in the same beaker and preserve the filtrate (B).

5.2.1.4 Transfer the filter with its residue into a previously weighed platinum crucible and char the filter paper at a low heat without burning the paper. Finally ignite at 900° to 950°C to a constant mass. Moisten the residue with few millilitres of dilute sulphuric acid (1:1) and add to it about 10 ml of hydrofluoric acid. Evaporate to dryness, ignite and cool.

5.2.1.5 Fuse thoroughly the residue 5.2.1.4 left over in the platinum crucible, after volatilization of silica with 1 to 2 g of fusion mixture and add the extract in dilute hydrochloric acid to the filtrate reserved under 5.2.1.3. Mix these combined filtrates with that reserved under 5.2.1.1. Transfer the final filtrate to 250 ml volumetric flask and make up to the main solution volume. (If filtrate is bulky, it should be concentrated to 250 ml by boiling). Suitable aliquots are taken for determination of ferric oxide, alumina, calcium oxide and magnesia.

5.2.2 For Magnesite Refractory Materials

5.2.2.1 Weigh one gram of the sample in a platinum crucible and fuse it with 6 to 8 g of pure anhydrous sodium carbonate. Extract the melt carefully with 40 to 50 ml of dilute hydrochloric acid in a 500 ml beaker and when dissolution is complete, wash the crucible thoroughly with hot water. Evaporate the solution to dryness on hot-plate and bake for about 20 minutes.

5.2.2.2 Cool the beaker, add 25 to 30 ml of dilute hydrochloric acid, boil and filter. Transfer thoroughly all the residue in the beaker to the filter by a jet of hot water and wash it free from acid by means of hot water. Collect the filtrate and washings in the same beaker and preserve it. Further, complete the estimation as described under 5.2.1.2 to 5.2.1.5.

6 DETERMINATION OF FERRIC OXIDE BY THE SPECTROPHOTOMETRIC METHOD

6.1 Outline of the Method

Iron (III) in the aliquot from the main solution is reduced to iron (II) with hydroxylamine hydrochloride and treated with *O*-phenanthroline. The orange red complex produced is measured at 510 nm. The amount of iron (as Fe_2O_3) is evaluated from the calibration curve obtained under similar conditions.

6.2 Reagent

6.2.1 *Para*-nitrophenol Indicator Solution, 1 percent.

6.2.2 Tartaric Acid Solution, 10 percent (*m/v*).

6.2.3 Dilute Ammonia Solution, 1 : 3 (*v/v*).

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

6.2.5 Hydroxylamine Hydrochloric, 10 percent (*m/v*).

6.2.6 Standard Iron Solution (1 ml = 0.0001 g of Fe_2O_3).

Dissolve 0.7024 g of ferrous ammonium sulphate in water, add 5 ml of concentrated H_2SO_4 and oxidize with bromine water. Boil to expel excess bromine. Cool and make up to 1 litre.

6.3 Procedure

6.3.1 Take 100 ml aliquot of main solution in 5.2.1.5 into 250-ml volumetric flask. Add few drops of paranitrophenol indicator and 25 ml of tartaric acid solution. Neutralize the solution with ammonia solution. Acidify the solution with dilute hydrochloric acid to pH 4.0 to 4.5. Add 20 ml of hydroxylamine hydrochloride and 25 ml of *O*-phenanthroline and make up. Allow to stand for 1 h and measure the absorbance at 510 nm against reagent blank prepared by using same quantity of reagents as used for sample.

6.3.2 Calibration

Draw a calibration curve by taking 0, 10, 20, 30, 40, and 50 ml of standard iron solution into six 250 ml volumetric flasks and proceed in accordance with 6.3.1 and measure the absorbance at 510 nm against reagent blank. Plot the absorbance values against mg of Fe_2O_3 per 250 ml of the solution.

6.3.3 Calculation

Convert the spectrophotometric readings of sample to mg of Fe_2O_3 by means of calibration curve and calculate Fe_2O_3 as follows:

$$\text{Fe}_2\text{O}_3, \text{ percent by mass} = \frac{A}{B} \times \frac{1}{10}$$

where

A = mass in mg, of Fe_2O_3 , found in aliquot of the solution, and

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

7 DETERMINATION OF ALUMINA BY EDTA METHOD

7.1 Outline of the Method

A suitable aliquot of the main solution is taken in a beaker and 0.05 M EDTA is added in excess. pH is adjusted at 5.8 when EDTA will form complex with mixed oxides i. e. R_2O_3 (Al_2O_3 , Fe_2O_3 , TiO_2) percent in the solution. In the first titration excess EDTA is titrated against standard zinc acetate solution using xylenol orange as indicator. Same solution is boiled with sodium fluoride when EDTA complexed with alumina is released and titrated against standard zinc acetate solution. Alumina can be determined from the second titration. If titanium is present in the sample, equivalent amount of EDTA corresponding to titanium is deducted from the second titration and the remaining quantity of EDTA will correspond to alumina.

7.2 Reagents

7.2.1 Xylenol Orange (0.5 percent)

Dissolve 0.5 g of xylenol orange in 100 ml water. Add 2 drops of dilute hydrochloric acid (1:1).

7.2.2 Methyl Orange

Dissolve 0.05 g of indicator in 100 ml water.

7.2.3 EDTA (0.05M)

Dissolve 18.613 g of disodium dihydrogen ethylenediaminetetra acetate in one litre of water.

7.2.4 Zinc Acetate Solution

Dissolve 27.4 g of zinc acetate in 200 ml of water, add 1.3 ml of glacial acetic acid and 73 ml of sodium acetate buffer and make the volume to 2.5 litres.

7.2.4.1 Standardization of zinc acetate solution

Transfer 20 ml of standard EDTA solution (7.2.3) in 250 ml beaker and add 15 ml buffer. Titrate against zinc acetate solution using xylenol orange as indicator till the colour changes from yellow to red.

Calculate the normality of zinc acetate as follows:

$$N = \frac{20 \times 0.05}{V}$$

where V is volume of zinc acetate in ml.

7.2.5 Ammonia Solution. 1:1 (v/v)

7.2.6 Buffer Solution pH (5.8)

Dissolve 43 g of sodium acetate in 500 ml of distilled water, and 2 ml of glacial acetic acid and make the volume to one litre.

7.2.7 Sodium Fluoride — Solid

7.3 Procedure

7.3.1 First Titration

Take suitable aliquot say 25 or 50 ml of the main solution (5.2.1.5) in 250 ml beaker and add 20 ml of EDTA (0.05 M). Stir well. Add 1 to 2 drops of methyl orange indicator. Add ammonia solution (1:1) till just alkaline. Add 15 ml of buffer solution and boil for about 5 to 10 minutes. Cool, add about 3 to 4 drops of xylenol orange indicator and titrate with standard zinc-acetate solution till colour changes from yellow to red.

7.3.2 Second Titration

Add about 2 g of sodium fluoride in the above solution (7.3.1) and boil for 5 to 10 minutes, cool and add 15 ml of buffer solution. Add about 2-3 drops of xylenol orange indicator and titrate against standard zinc acetate solution, till colour changes from yellow to red. Note the volume (v) of zinc acetate used.

7.4 Calculation

Aluminium oxide (Al_2O_3),

$$\text{percent by mass} = \frac{V}{m} \times \frac{N \times 50.98 \times 100}{1000}$$

where

V = volume of zinc acetate in ml, required to titrate liberated EDTA, calculated from second titration (7.3.2); and

m = mass in g, of the sample taken.

NOTE — In case titanium is present, calculate the Al_2O_3 content as follows:

$$\begin{aligned} & \text{Aluminium oxide (Al}_2\text{O}_3 \text{), percent by mass} \\ &= \frac{v - v_1}{m} \times \frac{N \times 50.98 \times 100}{1\ 000} \end{aligned}$$

where

v_1 = volume in ml, of EDTA equivalent to the percent by mass of titanium dioxide (TiO₂) in the sample.

8 DETERMINATION OF CALCIUM OXIDE BY EDTA METHOD

8.1 Outline of the Method

A suitable aliquot of the main solution is titrated against standard EDTA using Patton and Reeder's indicator at pH 12. The colour change from wine red to clear blue indicates the end point.

8.2 Reagents

8.2.1 Glycerol, 1 : 1 (v/v).

8.2.2 Triethanolamine, liquid.

8.2.3 Diethylamine

8.2.4 Sodium Hydroxide Solution, 4 N.

Dissolve 80 g of sodium hydroxide in a 500 ml volumetric flask. Make up to the mark with water.

8.2.5 Patton and Reeder's Indicator

Grind 100 mg of the indicator with 10 g of sodium or potassium sulphate until a homogeneous mixture is obtained. Store in an air-tight bottle.

8.2.6 Concentrated Nitric Acid, rd = 1.42 (conforming to IS 264 : 1976).

8.2.7 Potassium Periodate, solid.

8.3 Procedure

8.3.1 Take 10 ml of main solution 5.2.1.5 of the sample in a 250 ml conical flask. Add 5 ml of glycerol with constant stirring and 2 ml of triethanolamine/diethylamine to this, add 10 to ml of NaOH (4N) and shake well to adjust the pH 12 or slightly more. Add approximately 50 ml of water and 50 mg of solid Patton and Reeder's indicator. Titrate against EDTA solution 0.01 M till one drop of EDTA produces a sharp change in colour from wine red to greenish blue.

8.3.2 Alternate procedure to be followed when manganese is present in high amounts.

Take 10 ml of main solution (see 5.2.1.5) into a 250 ml conical flask. Add 2 to 3 drops of nitric acid followed by 50 mg of potassium periodate. Keep the flask on water-bath till a pink colour develops. Shake and allow to cool to room temperature. Add 5 ml of glycerol with constant stirring and then 2 ml of diethylamine/Triethanolamine. Add few drops of sodium hydroxide solution and shake well to adjust the pH 12 or slightly more. Add approximately 50 ml of water and 100 mg of solid Patton and Reeder's indicator and titrate against 0.01 M EDTA solution. The end point of the titration is reached when one to two drops of EDTA produces a sharp change in colour from violet to blue.

8.4 Calculations

$$\begin{aligned} 1 \text{ ml of } 0.01 \text{ M EDTA} &= 0.5608 \text{ mg CaO} \\ \text{calcium oxide (CaO),} & \\ \text{percent by mass} &= \frac{0.5608 \times v}{m} \end{aligned}$$

where

v = volume in ml, of EDTA used; and
 m = mass in g, of sample taken.

9 DETERMINATION OF MAGNESIUM OXIDE BY EDTA METHOD

9.1 Outline of the Method

A suitable aliquot of the main solution 5.2.1.5 is titrated at pH 10 against standard EDTA solution using triethanolamine for overcoming interference due to iron and aluminium and with thymolphthalexone as indicator. The titre value gives the sum of calcium and magnesium present in the solution from which the value corresponding to magnesium is obtained by subtracting that of calcium.

9.2 Reagents

9.2.1 Triethanolamine, 1:1 (v/v)

9.2.2 Buffer Solution (pH 10), As per 7.2.5.

9.2.3 Thymol Phthalexone Indicator, 1.0 percent (v/v)

Grind 100 mg of thymol phthalexone indicator with 10 g of potassium nitrate. Store it in an air-tight container.

9.2.4 Standard EDTA Solution, as per 7.2.7.**9.3 Procedure**

9.3.1 Take out 25 ml of main solution 5.2.1.5 and add to it 5 ml of triethanolamine (1 : 1) with constant shaking and 20 ml of buffer solution of pH 10. Add 50 mg of the solid thymolphthalexone indicator followed by approximately 50 ml of water. Titrate against standard EDTA solution until the colour changes from blue to clear pink.

9.4 Calculations

1 ml of 0.01 M EDTA = 0.403 2 mg of MgO

Magnesium oxide (MgO),
percent by mass = $\frac{(v_1 - v) \times 0.403 2}{m}$

where

v_1 = volume in ml, of EDTA used in MgO titration;

v = volume in ml, of EDTA used in CaO determination; and

m = mass in g, of the sample taken.

Bureau of Indian Standards

BIS is a statutory institution established under the *Bureau of Indian Standards Act, 1986* to promote harmonious development of the activities of standardization, marking and quality certification of goods and attending to connected matters in the country.

Copyright

BIS has the copyright of all its publications. No part of these publications may be reproduced in any form without the prior permission in writing of BIS. This does not preclude the free use, in the course of implementing the standard, of necessary details, such as symbols and sizes, type or grade designations. Enquiries relating to copyright be addressed to the Director (Publication), BIS.

Review of Indian Standards

Amendments are issued to standards as the need arises on the basis of comments. Standards are also reviewed periodically; a standard along with amendments is reaffirmed when such review indicates that no changes are needed; if the review indicates that changes are needed, it is taken up for revision. Users of Indian Standards should ascertain that they are in possession of the latest amendments or edition by referring to the latest issue of 'BIS Handbook' and 'Standards Monthly Additions'.

This Indian Standard has been developed from Doc: No. MTD 29 (3802)

Amendments Issued Since Publication

Amend No.	Date of Issue	Text Affected

BUREAU OF INDIAN STANDARDS

Headquarters:

Manak Bhavan, 9 Bahadur Shah Zafar Marg, New Delhi 110002
Telephones: 323 01 31, 323 83 75, 323 94 02

Telegrams: Manaksanstha
(Common to all offices)

Regional Offices:

Central : Manak Bhavan, 9 Bahadur Shah Zafar Marg
NEW DELHI 110002

Telephone
323 76 17, 323 38 41

Eastern : 1/14 C.I.T. Scheme VII M, V.I.P. Road, Maniktola
CALCUTTA 700054

{ 337 84 99, 337 85 61
{ 337 86 26, 337 91 20

Northern : SCO 335-336, Sector 34-A, CHANDIGARH 160022

{ 60 38 43
{ 60 20 25

Southern : C.I.T. Campus, IV Cross Road, MADRAS 600113

{ 235 02 16, 235 04 42
{ 235 15 19, 235 23 15

Western : Manakalaya, E9 MIDC, Marol, Andheri (East)
MUMBAI 400093

{ 832 92 95, 832 78 58
{ 832 78 91, 832 78 92

Branches : AHMADABAD. BANGALORE. BHOPAL. BHUBANESHWAR.
COIMBATORE. FARIDABAD. GHAZIABAD. GUWAHATI.
HYDERABAD. JAIPUR. KANPUR. LUCKNOW. PATNA.
THIRUVANANTHAPURAM.