

भारतीय मानक प्रारूप  
चूना पत्थर, डोलोमाइट एवं सम्बद्ध सामग्री का  
रासायनिक विश्लेषण

भाग 3 लौह ऑक्साइड, एलुमिना, कैल्शियम ऑक्साइड, एवं मैग्नीशिया ज्ञात करना  
(दूसरा पुनरीक्षण)

*Draft Indian Standard*

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

ICS 73.080

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Methods of Chemical Analysis of Metals Sectional Committee, MTD 34

## FOREWORD

This draft Indian Standard (Part 3) (Second Revision) subject to its finalization, is to be adopted by the Bureau of Indian Standards on recommendation of the Methods of Chemical Analysis of Metals Sectional Committee and approval of the Metallurgical Engineering Division Council.

This standard was first published in 1962 and 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. Subsequently, the first revision was issued to bifurcate this standard into different parts covering determination of each element in separate parts. This revision has been brought out to bring the standard in the latest style and format of the Indian Standards. 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 4 Determination of carbon dioxide

Part 5 Determination of chlorides

Part 6 Determination of free silica

In this part the following changes have been made:

- a) The determination of ferric oxide by calorimetric method (for iron content  $\leq 0.5$  percent) and the permanganate method (for iron content  $\geq 0.5$  percent) has been replaced by spectrophotometric method.
- b) The determination of alumina by 'oxine method' has been replaced by 'EDTA method'.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to minerals other than magnesite) and by 'the pyrophosphate method' (applicable to dolomite and limestone) has been replaced by 'EDTA method'.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oxide in magnesite by 'the phosphate method' and determination of magnesium oxide in calcite by 'the oxine method' have been replaced by EDTA method.

For the purpose of deciding whether a particular requirement of this standard is complied with, the final value, observed or calculated, expressing the result of a test or analysis, shall be rounded off in accordance with IS 2 : 2022 'Rules for rounding off numerical values (*second revision*)'. The number of significant places retained in the rounded off value should be same as that of the specified value in this standard.

*Draft Indian Standard*CHEMICAL ANALYSIS OF LIMESTONE,  
DOLOMITE AND ALLIED MATERIALSPART 3 DETERMINATION OF IRON OXIDE, ALUMINA,  
CALCIUM OXIDE AND MAGNESIA*(Second 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 (Percent by Mass)</i>
Iron oxide ( Fe <sub>2</sub> O <sub>3</sub> )	0.2 to 2
Alumina ( Al <sub>2</sub> O <sub>3</sub> )	0.2 to 2
Calcium oxide ( CaO )	0.5 to 55
Magnesium oxide ( MgO )	0.2 to 52

**2 REFERENCES**

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

<i>IS No.</i>	<i>Title</i>
264 : 2005	Nitric Acid – Specification ( <i>third revision</i> )
1070 : 1992	Reagent grade water – Specification ( <i>third 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.

**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 ± 2°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) 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 **5.2.1.5**

## **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  $\text{Fe}_2\text{O}_3$  ) 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  $\text{Fe}_2\text{O}_3$ ).

Dissolve 0.7024 g of ferrous ammonium sulphate in water, add 5 ml of concentrated  $\text{H}_2\text{SO}_4$  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 0-phenthroline 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<sub>2</sub>O<sub>3</sub> per 250 ml of the solution.

### 6.3.3 Calculation

Convert the spectrophotometric readings of sample to mg of Fe<sub>2</sub>O<sub>3</sub> by means of calibration curve and calculate Fe<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>O<sub>3</sub> ( Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> ) 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 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

$$\text{Aluminium oxide (Al}_2\text{O}_3\text{), percent by mass} = \frac{V}{m} \times \frac{N \times 50.98 \times 100}{1000}$$

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  $\text{Al}_2\text{O}_3$  content as follows:

$$\text{Aluminium oxide (Al}_2\text{O}_3\text{), percent by mass} = \frac{V - V_1}{m} \times \frac{N \times 50.98 \times 100}{1000}$$

where

$V_1$  = volume in ml, of EDTA equivalent to the percent by mass of titanium dioxide ( $TiO_2$ ) 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).

**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 Reader'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

1 ml of 0.01 M EDTA = 0.5608 mg CaO

calcium oxide (CaO), percent by mass =  $\frac{0.5608 \times v}{m}$

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 = 0.4032 mg of MgO

Magnesium oxide (MgO), percent by mass =  $\frac{(v_1 - v) \times 0.4032}{m}$

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.