

भारतीय मानक मसौदा
रासायनिक उद्योग के लिए चूना पत्थर — विशिष्टि
(IS 3204 का दूसरा पुनरीक्षण)

Draft Indian Standard
Limestone for Chemical Industry— Specification
(*Second Revision of IS 3204*)

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ICS 71.060.50

Inorganic Chemicals Sectional Committee, CHD 01

Last date of comments: 25.06.2024

Inorganic Chemicals Sectional Committee, CHD 01

FOREWORD

(*Formal clauses will be added later*)

This standard was originally published in 1965 and subsequently revised in 1978. In the first revision changes were made in the methods of determination of manganese, sulphur and phosphorus in the light of experience gained during these years.

In this revision, instrumental test methods for the determination of calcium, iron, magnesium and manganese have been added as alternate test methods. In addition to this, editorial corrections have been made wherever required. Also, Reference clause has been incorporated. Further, Packing and Marking clause has been updated.

Limestone is an important basic raw material for the chemical industry. It is widely distributed throughout India. Almost every state possesses limestone deposits of various degrees of purity. The chemical industry uses relatively small quantities of limestone as compared to quicklime and hydrated lime, although many industries can use both these materials.

Physical requirements, such as specific gravity, porosity, compressive strength and size of stone are not included in this standard, as these requirements will depend on, amongst others, the types of kilns used for burning limestone.

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 the same as that of the specified value in this standard.

Draft Indian Standard
LIMESTONE FOR CHEMICAL INDUSTRY— SPECIFICATION
(*Second Revision*)

1 SCOPE

1.1 This standard prescribes the requirements and the methods of sampling and test for limestone for chemical industry. It also covers seashells and calcite, a crystalline form of naturally occurring calcium carbonate.

1.1.1 This standard does not cover limestone for building, agricultural, metallurgical, glass and ceramic industries.

2 REFERENCES

The standards listed in Annex A contain provisions which through reference in this text, constitute provisions 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 Indian Standard are encouraged to investigate the possibility of applying the most recent editions of these standards.

3 GRADES

The limestone shall be of the following four grades depending upon their suitability for various uses on the basis of their chemical properties:

Grade 1 — suitable for the manufacture of bleaching powder, bleach liquor, textiles, varnishes, pulp and paper.

Grade 2 — suitable for the manufacture of soda ash by the Solvay process, caustic soda by the lime-soda process.

Grade 3 — suitable for the manufacture of calcium carbide.

Grade 4 — suitable for sugar manufacture.

4 REQUIREMENTS**4.1 Description**

The material shall be in the form of lumps, free from dirt and added impurities.

4.2 The material shall comply with the requirements given in Table 1

When tested according to the methods prescribed in IS 1760 and in Annex B of this standard. Reference to the relevant test methods is given in col 7 and 8 of the table.

5 PACKING AND MARKING**5.1 Packing**

The material shall be supplied in open wagons, or as agreed to between the purchaser and the supplier.

5.2 Marking

A metallic or cardboard label of appropriate size bearing the following information with suitable paint or ink shall be conspicuously displayed on the carrier and also placed inside:

- a) Name and grade of the material;
- b) Name of the supplier and his recognized trade-mark, if any;
- c) Gross and net mass;
- d) Batch number; and
- e) Date of supply.

Table 1 Requirements for Limestone for Chemical Industry

(Clauses 4.2 and 6.2.2)

Sl. No.	Characteristic	Requirement				Method of Test Ref to in	
		Grade 1	Grade 2	Grade 3	Grade 4	Annex B	IS
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
i)	Loss on ignition, percent by mass, <i>Max</i>	46.0	46.0	46.0	44.0	—	1760 (Part 1)
ii)	Silica (as SiO ₂), percent by mass, <i>Max</i>	0.75	—	1.0	2.0	—	1760 (Part 2)
iii)	Iron (as Fe ₂ O ₃), percent by mass, <i>Max</i>	0.15	—	0.25	—	B-5	1760 (Part 3)
iv)	Calcium (as CaO) percent by mass, <i>Min</i>	54.0	53.0	54.0	50.0	B-5	1760 (Part 3)
v)	Magnesium (as MgO), percent by mass, <i>Max</i>	2.0	1.0	0.8	1.0	B-5	1760 (Part 3)
vi)	Manganese (as Mn ₂ O ₃), percent by mass, <i>Max</i>	0.06	—	—	—	B-2 or B-5	—
vii)	Carbon dioxide (as CO ₂), percent by mass, <i>Min</i>	42.0	42.0	42.0	41.0	—	1760 (Part 4)
viii)	Sulphur (as S), percent by Mass, <i>Max</i>	—	—	0.1	—	B-3	—
ix)	Phosphorus (as P), percent by mass, <i>Max</i>	—	—	0.01	—	B-4	—
x)	Alumina (as Al ₂ O ₃) and ferric oxide as (Fe ₂ O ₃) together, percent by mass, <i>Max</i>	—	—	0.5	1.5	—	1760 (Part 3)
xi)	Silica (as SiO ₂), alumina (as Al ₂ O ₃), and ferric oxide (as Fe ₂ O ₃),) together, percent by mass, <i>Max</i>	—	3.0	—	—	—	1760 (Part 1) and 1760 (Part 3)

5.2.1 BIS Certification Marking

The product(s) conforming to the requirements of this standard may be certified as per the conformity assessment schemes under the provisions of the *Bureau of Indian Standards Act, 2016* and the Rules and Regulations framed thereunder, and the products may be marked with the standard mark.

6 SAMPLING**6.1 Preparation of Test Samples**

The method for drawing representative samples of the material shall be as prescribed in IS 2109.

6.2 Number of Tests

6.2.1 Tests for determination of loss on ignition, silica and calcium shall be carried out on each of the individual samples.

6.2.2 Tests for the determination of the remaining characteristics given in Table 1 shall be performed on the composite sample.

6.3 Criteria for Conformity

6.3.1 For Individual Samples

For those characteristics which are tested on individual samples, the mean and the range of test results shall be computed as follows:

$$\text{Mean } (\bar{X}) = \frac{\text{sum of individual test results}}{\text{Number of test results}}$$

Range (R) = Difference between the maximum and the minimum values of test results

For declaring the conformity of the lot:

$\bar{X} + 0.6 R$ shall be less than or equal to the maximum specified requirement, or

$\bar{X} - 0.6 R$ shall be greater than or equal to the minimum specified requirement.

6.3.2 For Composite Sample

For declaring the conformity of the lot to the requirements of all characteristics tested on the composite sample, the test results shall satisfy the corresponding specified requirements.

ANNEX A

(Clause 2)

(LIST OF REFERRED STANDARDS)

<i>IS No.</i>	<i>Title</i>
IS 296 : 1986	Specification for sodium carbonate, anhydrous (<i>third revision</i>)
IS 574 : 1989	Glassy sodium metaphosphate specification (<i>fourth revision</i>)
IS 1070 : 2023	Reagent grade water — Specification (<i>fourth revision</i>)
IS 1760 (Part 1) : 1991	Chemical analysis of limestone, dolomite and allied materials: Part 1 determination of loss on ignition (<i>first revision</i>)
IS 1760 (Part 2) : 1991	Chemical analysis of dolomite and allied: Part 2 determination of limestone, materials silica (<i>first revision</i>)
IS 1760 (Part 3) : 1992	Chemical analysis of limestone, dolomite and allied materials: Part 3 determination of iron oxide, alumina, calcium oxide and magnesia (<i>first revision</i>)
IS 1760 (Part 4) : 1991	Chemical analysis of limestone, dolomite and allied materials: Part 4 determination of carbon dioxide (<i>first revision</i>)
IS 2109 : 1982	Methods of sampling dolomite, limestone and other allied materials (<i>first revision</i>)
IS 3025(Part 2) : 2019/ISO 11885	Methods of sampling and test (physical and chemical) for water and wastewater: Part 2 determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP - OES) (<i>first revision</i>)
IS 4161 : 2023	Nessler cylinder — Specification (<i>first revision</i>)

ANNEX B

(Clause 4.2 and Table 1)

METHODS OF TEST FOR LIMESTONE FOR CHEMICAL INDUSTRY

B-1 QUALITY OF REAGENTS

B-1.1 Unless specified otherwise, pure chemicals and distilled water (*see* IS 1070) shall be employed in tests.

NOTE – ‘Pure chemicals’ shall mean chemicals that do not contain impurities which effect the results of analysis.

B-2 MANGANESE

B-2.1 Outline of the Method

Manganese is determined colorimetrically by visual comparison.

B-2.2 Apparatus

B-2.2.1 Platinum Crucible

B-2.2.2 Nessler Cylinders — 100 ml capacity (*see* IS 4161).

B-2.3 Reagents

B-2.3.1 Dilute Nitric Acid — 1 : 1 (v/v).

B-2.3.2 Sodium Carbonate — see IS 296.

B-2.3.3 Dilute Phosphoric Acid — 1 : 1 (v/v) .

B-2.3.4 Potassium Periodate — solid.

B-2.3.5 Standard Manganese Solution

Dissolve 0.1 g of pure electrolytic grade of manganese in dilute nitric acid, boil off nitrous fumes and make up the volume to 1 000 ml mark in a volumetric flask. One millilitre of this solution is equivalent to 0.1 mg of manganese (as Mn).

B-2.4 Procedure

Weigh accurately about 1 g of the material and dissolve in about 25 ml of dilute nitric acid. Filter and wash the residue with hot water. Ignite the residue in a platinum crucible, fuse with a little sodium carbonate, dissolve in dilute nitric acid and add to the main filtrate. To the solution (if necessary, filtered) add 20 ml of dilute phosphoric acid and 0.6 g to 0.8 g of potassium periodate. Heat the solution to boiling and keep at boiling point for about 10 min (one hour for very small amounts). Cool the solution to room temperature. Transfer the solution completely to a Nessler cylinder and make up the volume to 100 ml mark. Simultaneously take 20 ml of dilute phosphoric acid and 0.6 g to 0.8 g of potassium periodate in another beaker and add 4.2 ml of standard manganese solution. Heat the solution and boil as above. Cool and transfer to another Nessler cylinder and make up the volume to 100 ml.

B-2.5 The material shall be deemed to have passed the requirement of the test if the colour produced in the test with the material is equal to or less than that product in the control test.

B-2.6 Alternative Method

Manganese may alternatively be determined by ICP-OES instrumental test method as prescribed at **B-5**.

B-3 SULPHUR

B-3.1 Outline of the Method

Sulphur is oxidized with bromine water and then precipitated as barium sulphate by addition of barium chloride solution.

B-3.2 Apparatus

B-3.2.1 Platinum Crucible

B-3.2.2 Muffle Furnace

B-3.3 Reagents

B-3.3.1 Sodium Carbonate — see IS 296.

B-3.3.2 Bromine water — saturated solution.

B-3.3.3 Dilute Hydrochloric Acid — 1 : 1 (v/v).

B-3.3.4 Methyl Red Indicator Solution — dissolve 0.15 g of methyl red 500 ml of water.

B-3.3.5 Dilute Ammonium Hydroxide — 1 : 1 (v/v).

B-3.3.6 Barium chloride Solution — 10 percent (m/v).

B-3.4 Procedure

Weigh accurately about 2.5 g of the finely powdered material in a platinum crucible and mix it with 10 g of sodium carbonate. Place the crucible in a furnace and gradually raise the temperature of the furnace to 800 °C. Keep the crucible for half an hour at this temperature and finally raise to 1 000 °C for fusion. Cool and place the crucible in a 250 ml beaker and cover with hot water. Boil till the melt breaks down completely to powder. If necessary, hasten the process by crushing any lumps with a glass rod. When no lumps are left, filter through a fast filter paper and wash

well with hot water containing about 1 percent sodium carbonate. Reject the residue and evaporate the total filtrate to about 150 ml, after adding 10 ml of bromine water and 90 ml of dilute hydrochloric acid. During this all excess bromine will be expelled. Add a few drops of methyl red indicator and make it alkaline with dilute ammonium hydroxide. Boil and filter, washing with hot water. To the filtrate add 5 ml of dilute hydrochloric acid, dilute to about 200 ml and boil. To the boiling solution, add slowly, with constant stirring, 10 ml of hot barium chloride solution. Allow the precipitate to stand overnight. Filter through a filter paper or Gooch crucible and ignite at 800 °C to constant mass.

B-3.4.1 Carry out a blank determination simultaneously using the same quantities of all the reagents.

$$\text{Sulphur, percent by mass} = \frac{13.74 \times (M_1 - M_2)}{M}$$

where

M_1 = mass in g of the barium sulphate precipitate obtained from the material,

M_2 = mass in g of the barium sulphate precipitate obtained from the blank, and

M = mass in g of the material taken for the test.

B-4 PHOSPHORUS

B-4.1 Dissolve 2 g of the material in 20 ml of dilute hydrochloric acid (1 : 1, v/v) with a few drops of concentrated nitric acid. Filter and proceed with the filtrate according to method prescribed in **B-4** of IS 574.

B-5 DETERMINATION OF IRON, CALCIUM, MANGANESE AND MAGNESIUM BY INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROMETER (ICP-OES) METHOD

B-5.1 Principle

The sample solution under analysis is nebulized through a nebulizer inside a spray chamber. The aerosol formed is aspirated to argon plasma torch [produced by a radio-frequency inductively coupled plasma (ICP)], where the molecules break into constituent atoms and/or molecular species and atoms are get excited. These excited atoms then return back to the lower energy state by emitting radiation of specific wavelength. These emitted radiations are characteristic of an element and are measured by the Photomultiplier tube detector and intensity of such emitted radiation is directly proportional to the concentration of respective constituent element in the sample.

B-5.2 Recommended Wavelength, limit of quantification and important spectral interferences

Elements along with the recommended wavelengths and typical estimated limits of quantification are listed in Table 2. Actual working detection limits are dependent on the type of instrumentation, detection device and sample introduction system used and on the sample matrix. Therefore, these concentrations can vary between different instruments.

Additionally, Table 2 lists the most important spectral interferences at the recommended wavelengths for analysis.

Table 2 Recommended Wavelengths, Achievable Limits of Quantification for Different Configuration of Instruments and Important Spectral Interferences

(Clauses B-5.2 and B-5.4)

Sl No.	Element	Wavelength (nm)	Approximately Achievable Limits		Interfering Elements
			Radial Viewing (µg)	Axial Viewing (µg)	
(1)	(2)	(3)	(4)	(5)	(6)

i)	Fe	238.204	14	(3)	Co
		259.940	6	2	Co
		271.441	-	-	-
ii)	Ca	315.887	100	13	Co, Mo
		317.933	26	4	Fe, V
		393.366	0.4	25	V, Zr
		422.673	-	-	V, Mo, Zr
iii)	Mg	279.078	33	19	Fe
		279.553	1	7	Fe
		285.213	4	14	Cr
iv)	Mn	257.610	1	0.4	Cr, Fe, Mo, W
		293.305	(20)	8	Al, Cr, Fe, Ti

B-5.3 Reagents and Solutions

B-5.3.1. Nitric Acid (65 percent) Suprapure

B-5.3.2 Standard Stock Solution

Either Prepare by dissolving proportionate amount of soluble compounds of elements (preferably spectroscopic grade), or use commercially available certified stock solution of 10, 100 or 1 000 µg/ml of Lead, Iron, calcium, magnesium, manganese, arsenic, molybdenum, aluminium and mercury in 2 to 5 percent nitric acid. It is preferable to prepare single stock solution of multi elemental standards for analysis.

B-5.3.3 Standard solution

Pipette out 5 ml from 100 µg/ml standard stock solution into a 100 ml volumetric flask & make up volume with 2 percent nitric acid to prepare 5 µg/ml solution. From this 5 µg/ml solution, an aliquot of 1.0 ml, 3.0 ml and 5.0 ml taken in 50 ml volumetric flasks (separate) and make up volume with 2 percent nitric acid to prepare 0.1 µg/ml, 0.3 µg/ml and 0.5 µg/ml solution of respective elements under reference.

B-5.3.4 Sample preparation

Weigh about 2.5 g of the sample in a 50 ml volumetric flask and add 1.0 ml nitric acid and make up the volume with water.

NOTE — Sample should be clear before injecting to the instrument.

B-5.3.5 Reagent Blank Solution

Place 50 ml of nitric acid and 1 000 ml of water into an HDPE or PP container. For ultra-trace analysis, polytetrafluoroethylene (PTFE) containers should be used. Prior to analysis, make sure that the acid matrix and concentration of the reagent blank solution is the same as in the standard and sample solutions.

B-5.4 Instrument

Set up the instrument as per the manufacturer's instructions manual for recommended operating parameters, based on the manufacturers operating manual and evaluated by internal check analysis using of standard solution of element as well as data selected carefully from Table 2.

For analysis of mercury and arsenic, a gas (hydride)/vapour generating system is coupled with ICP, instead of using of nebulizer. The mercury vapour/arsine generated through the system is carried by the carrier gas (Ar) to plasma torch, and other instrumental conditions shall be the same as above.

NOTE — Sensitivity, instrumental detection limit, precision, linear dynamic range and interference effects will be investigated and established for each individual analyte line on that particular instrument.

B-5.5 Procedure

B-5.5.1 Calibration

Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures, using the intermediate mixed standard solutions (**B-5.3.5**). The relationship between concentration and intensity is linear up to six orders of magnitude. Examine the spectra of the element and make necessary adjustments (if required) for the exact peak positions and baselines to ensure proper measurements of the respective peak intensities. Flush the system with the reagent blank solution between each standard.

B-5.5.2 Before beginning the sample run, re-analyse the reference standard with the highest concentration as if it were a sample. Ensure that the concentration values do not deviate from the actual values by more than ± 5 percent (or the established control limits, whichever is lower). If they do, follow the recommendations of the instrument manufacturer to correct for this condition. Begin the sample run by flushing the system with the reagent blank solution between each sample. It is recommended to analyse a calibration check solution and the calibration blank solution every 10 samples. Analyze the sample solution and calculate the concentration in $\mu\text{g/ml}$ of the calcium (and/or Iron, magnesium and manganese) in the sample solution.

NOTE — It is recommended that IS 3025(Part 2) /ISO 11885 may be referred and practiced for ensuring precise and reproducible analysis.

B-5.6 Calculation

The mass concentrations for each element are determined with the aid of the instrument software by following steps.

- i) Relate emission signals from calibration blank and calibration solutions with the signals from reference elements and establish a calibration plot.
- ii) Determine the mass concentrations of samples with the aid of the emissions and the calibration graphs and calculate the quantity in mg/kg of the constituent elemental impurities in the sample, by multiplying the value by 20 (Dilution factor).