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*Draft Indian Standard*

**LIMESTONE AND DOLOMITE FOR GLASS AND CERAMIC  
INDUSTRY - SPECIFICATION**

*(Second Revision)*

*भारतीय मानक मसौदा*

**कांच और सिरेमिक उद्योग के लिए चूना पत्थर और डोलोमाइ - विशिष्टि**

**( दूसरा पुनरीक्षण )**

ICS 81.040.30

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Glass, Glassware & Laboratoryware Sectional Committee, CHD 10

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**FOREWORD**

(Formal clauses shall be added later)

This standard was first published in 1957. The Committee responsible for its preparation, however, felt that it would be more realistic to report the presence of silica as SiO<sub>2</sub> and lime and magnesia as CaO and MgO respectively, to obtain a practical assessment of the constitution of the material. Further, with the publication of IS 1760: 1962 'Methods of chemical analysis of limestone, dolomite and allied materials' in which methods have been prescribed which shall be useful as referee methods, the Committee decided to incorporate in the first revision in 1973, method of rapid analysis based on the use of EDTA to make this standard more useful to the glass factories and the suppliers of the materials in keeping control on the quality of the product.

In this third revision, the instrumental methods have been added and several editorial changes such as inclusion of ICS No., Hindi title and Reference clause have also been incorporated.

In this standard separate limits for iron content (as Fe<sub>2</sub>O<sub>3</sub>) have been prescribed for calcite, limestone and dolomite. Limits for lime (as CaO) have not been prescribed separately for dolomitic limestone and dolomite but have been left for agreement between the purchaser and the supplier subject to the total lime and magnesia content being in conformity with the

requirements given in Table 1. A method for the determination of loss on ignition has also been prescribed in the standard to enable one to have an idea of the nature of the material.

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.

# LIMESTONE AND DOLOMITE FOR GLASS AND CERAMIC INDUSTRY - SPECIFICATION (Second Revision)

## 1 SCOPE

**1.1** This standard prescribes requirements and methods of sampling and test for limestone and dolomite for glass industry for making colourless glass and dolomite used for manufacture of ceramic whitewares.

**1.2** Inferior grades of the material containing higher percentage of iron and used for making certain types of coloured glasses are not covered in this standard.

## 2 REFERENCES

The standards listed below contain provisions which through reference in this text, constitute provisions of and necessary adjuncts to 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.

<i>IS No.</i>	<i>Title</i>
264 : 2005	Nitric acid - Specification ( <i>third revision</i> )
266 : 1993	Sulphuric acid - Specification ( <i>third revision</i> )
1070 : 1992	Reagent Grade Water – Specification ( <i>third revision</i> )
2109 : 1982	Methods of sampling dolomite, limestone and other allied materials ( <i>first revision</i> )
2781 : 2020	Glossary of Terms Relating to Ceramicware ( <i>third revision</i> )

## 3 TERMINOLOGY

**3.1** For the purpose of this standard the definitions given in **IS 2781** shall apply.

**3.2** In this standard marble and calcite are covered under the term 'limestone', their iron content being generally less than that of limestone. Similarly, dolomitic limestone is covered under the term 'dolomite'.

## 4 REQUIREMENTS

**4.1 Description** — The material shall be in the form of lumps, aggregates or powder as agreed to between the purchaser and the supplier.

**4.2** The material, when tested in accordance with the methods prescribed in Annex A, shall comply with the requirements given in Table 1 and 2. Reference to relevant clauses of Annex A is given in col 4 of Table 1.

## 5 ADDITIONAL REQUIREMENTS FOR THE MATERIAL SUPPLIED IN THE FORM OF POWDER

**5.1 Moisture Content** — The material as received shall not contain more than **2.0** percent by mass of moisture when tested in accordance with **A-6**.

**5.2 Grain Size** — The grain size distribution of the material shall be between the following limits when tested in accordance with **A-7**:

a) Material retained on 2.00-mm IS Sieve: **Nil**

b) Material passing 125-micron IS Sieve, **15 percent by mass, Max**

NOTE — In case of a dispute, a mechanical sieve shaker shall be used.

**5.3** Moisture content and grain size shall be determined on laboratory sample (*see 6.1*).

### TABLE 1 REQUIREMENTS FOR LIMESTONE AND DOLOMITE FOR GLASS INDUSTRY

(Clause 4.2)

SL. No.	CHARACTERISTICS	REQUIREMENT (ON DRY BASIS)	METHOD OF TEST (REF TO CL NO. IN APPENDIX A)
(1)	(2)	(3)	(4)
i.)	silica (as SiO <sub>2</sub> ), percent by mass, <i>Max</i>	2.5	A-3
ii.)	Total iron (as Fe <sub>2</sub> O <sub>3</sub> ), percent by mass, <i>Max</i> in a) Calcite or marble b) Limestone c) Dolomitic limestone and dolomite	0.05 0.10 0.15	A-4
iii.)	Lime (as CaO), percent by mass, <i>Min</i>	<b>49</b>	A-5
iv.)	Total lime and magnesia (as CaO + MgO), percent by mass, <i>Min</i>	<b>50</b>	A-5

## 6 SAMPLING

**6.1 Laboratory Sample** — For the purpose of testing, a truly representative and homogeneous sample is essential. This shall be drawn and prepared in accordance with **IS 2109**.

**6.2 Test Sample** — Grind 5 to 10 g of the laboratory sample so that it passes through 15-micron IS Sieve. Dry to constant mass at  $105 \pm 2^\circ\text{C}$  and use it for the purpose of chemical analysis.

**ANNEX A**  
(Clause 4.2)

**METHOD OF TEST FOR LIMESTONE AND DOLOMITE**

**A-1 QUALITY OF REAGENTS**

A-1.1 Unless specified otherwise, pure chemicals and distilled water (*see* 1070) shall be used in the tests.

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

**A-2 LOSS ON IGNITION**

A-2.0 Loss on ignition is prescribed to be determined with a view to getting an idea of the nature of the material. This also helps in verifying the correctness of total of analysis results.

**A-2.1 Procedure** — Weigh accurately about 1 g of the test sample (*see* 5.2) in a tared platinum crucible. Cover with lid and heat gently for 5 minutes and then slowly raise the temperature to full heat over a period of 10 minutes. Transfer the crucible to a muffle furnace at  $1000 \pm 25^{\circ}\text{C}$  and heat to constant mass. Ignition for 30 minutes is usually sufficient. Determine the loss in mass and express the result as percentage of the mass of the material taken for the test.

**A-3. DETERMINATION OF SILICA**

**A-3.1 Reagents**

**A-3.1.1 Dilute Hydrochloric Acid** — 1:1 and 1:19 (v/v).

**A-3.1.2 Concentrated Hydrochloric Acid** — *See* IS 265.

**A-3.1.3 Sodium Carbonate Anhydrous** — *See* IS 296.

**A-3.1.4 Dilute Sulphuric Acid** — 1:1 (v/v).

**A-3.1.5 Hydrofluoric Acid** — 2:5 (v/v).

**A-3.2 Procedure**

**A-3.2.1** Weigh accurately about 1 g of the test sample (*see* 5.2) into a 250-ml beaker and add about 50 ml of water. Cover the beaker with a watch glass, and add 10 ml of concentrated hydrochloric acid through the spout of the beaker. Digest on a hot plate for about an hour and then boil for 10 minutes. Filter off the insoluble residue on a No. 40 Whatman filter paper or its equivalent. Wash the residue 4 to 5 times with hot water. Reserve the filtrate and washings for determination of silica.

**A-3.2.2** Transfer the filter paper with the residue to a platinum crucible and char the paper carefully. Burn off the carbon at a low temperature and then fuse the residue with 1 to 2 g of anhydrous sodium carbonate. Cool and dissolve the melt in dilute hydrochloric acid (1:1) and transfer quantitatively to the filtrate reserved for the determination of silica in **A-3.2.1**.

**A-3.2.3** Transfer the whole solution to an evaporating dish preferably of platinum and evaporate to dryness on a steam-bath, breaking up occasionally with a glass rod the crust of salts formed during evaporation. When the residue is completely dry and free from smell of hydrochloric acid, cover the dish with a clock glass and bake in an air-oven at 110°C for 1 hour. Cool the dish and its content and add 10 ml of concentrated hydrochloric acid followed by 20 ml of hot water. Stir the mixture with a glass rod. Cover the dish and digest the mixture on a steam-bath for 10 minutes without stirring. Filter through a No. 40 Whatman paper or its equivalent and rinse the dish with hydrochloric acid (1:19) scrubbing with a rubber tipped glass rod. Wash the precipitate five times with hot hydrochloric acid (1:19) and then with hot water until free from chloride. Reserve the paper with the residue. Reduce the volume of the filtrate and washings on a steam-bath and transfer back to the evaporating dish.

**A-3.2.4** Repeat the whole process of evaporation to dryness, baking at 110°C and filtration and washing in the same way as described in **A-3.2.3**. Preserve the filtrate and washings for determination of iron, lime and magnesia.

**A-3.2.5** Transfer the two filter papers with the residue to a tared platinum crucible and heat at a low flame to dry the residues and char the filter papers. Burn off the carbon completely at a low temperature and finally ignite the residue to constant mass preferably at 1100°C. Cool in a desiccator and weigh to obtain the mass of impure silica (A).

**A-3.2.6** Moisten the weighed residue with 10 drops of dilute sulphuric acid and add 5 ml of hydrofluoric acid. Evaporate to dryness on a sand bath taking care to avoid spurting. Ignite the residue again to constant mass, cool the crucible in a desiccator and weigh (B). Subtract the mass (B) of this residue from that of the impure silica (A) (*see* A-3.2.5) to obtain the mass of pure silica in the sample taken for the test.

**A-3.2.7** Carry out a blank determination following the same procedure and using the same amounts of reagents but without the sample and weigh the residue (C).

### **A-3.3 Calculation**

$$\text{Silica, percent by mass} = \left[ \frac{(A-B)-C}{D} \right] \times 100$$

Where,

A = mass in g of platinum crucible with impure silica before treatment with hydrofluoric acid (**A-3.2.5**);

B = mass in g of platinum crucible with residue, if any, after treatment with hydrofluoric acid (**A-3.2.6**);

C = mass in g of silica obtained in blank determination (**A-3.2.7**); and

D = mass in g of the sample taken for the test (**A-3.2.1**).

## **A-4. DETERMINATION OF IRON**

**A-4.0** — Iron is determined after the removal of silica by comparing the intensity of the red colour produced by the addition of ammoniumthiocyanate to the test solution and reference standard.

#### **A-4.1 Reagents**

**A-4.1.1 Concentrated Nitric Acid** — See IS 264.

**A-4.1.2 Concentrated Sulphuric Acid** — See IS 266.

**A-4.1.3 Ammonium Chloride**

**A-4.1.4 Ammonium Chloride Wash Solution** — Dilute 25 ml of concentratedhydrochloric acid, neutralize to methyl red with ammonium hydroxidesolution and dilute to 100 ml. Add 2 drops in excess of ammoniumhydroxide solution.

**A-4.1.5 Ammonium Hydroxide Solution** — relative density, about 0.90.

**A-4.1.6 Ammonium Nitrate Solution** — 1 percent (*m/v*).

**A-4.1.7 Methyl Red Indicator Solution** — Dissolve 0.15 g of methyl red in 500 ml of water.

**A-4.1.8 Ammonium Thiocyanate Solution** — approximately 5 percent (*m/v*).

**A-4.1.9 Standard Iron Solution** — Dissolve 0.4911 g of ferrous ammoniumsulphate [FeSO<sub>4</sub>(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>.6H<sub>2</sub>O] in water. Add 5 ml of concentrated sulphuric acid and 2 ml of concentrated nitric acid, boil, cool and makeup the volume to 1 000 ml in a volumetric flask. Pipette out 10 ml of this solution and dilute to 100 ml in a volumetric flask. One millilitre of this solution is equivalent to 0.01 mg of ferric oxide (as Fe<sub>2</sub>O<sub>3</sub>).

**A-4.2 Preparation of Solution for Test** — Fuse the residue in the platinum crucible obtained in **A-3.2.6** with 1 g of anhydrous sodiumcarbonate and dissolve the melt in hydrochloric acid (1:1). Transfer thesolution to that preserved in **A-3.2.4** for determination of iron, lime andmagnesia. Evaporate, if required, cool and make up the volume to 250 ml in a volumetric flask with water.

**A-4.3 Procedure** — Take 100 ml of the solution obtained in **A-4.2**. Add 2 ml of concentrated nitric acid and boil. From the boiling solution precipitate mixed oxides (R<sub>2</sub>O<sub>3</sub>) by carefully adding ammonium hydroxidesolution in the presence of ammonium chloride, using methyl red as indicator until the colour changes to a distinct yellow. Allow to settle and filter (Whatman No. 41 is suitable). Rinse the beaker and wash the precipitate 4 times with hot ammonium chloride wash solution and finally with hot ammonium nitrate solution until free from chloride. Preserve the filtrate and washings.

**A-4.3.1** Return the precipitate to the beaker and dissolve it by heating with 100 ml of water and 20 ml of concentrated sulphuric acid. Cool, transfer to 250-ml volumetric flask, rinsing the beaker with cold water and make up to the mark.

**A-4.3.2** Transfer 25 ml of the solution prepared in **A-4.3.1** to a 50-ml Nessler cylinder, add 5 ml of ammonium thiocyanate solution, dilute with water up to the mark and mix. Carry out a control test in another Nessler cylinder proceeding as above and using 2 ml, 4 ml and 6 ml of the standard iron solution for calcite, limestone and dolomite, respectively.

**A-4.3.3** The material shall be taken as not having exceeded the limit prescribed in Table 1, if the intensity of colour produced with the material is not greater than that produced in the control test.

## **A-5 DETERMINATION OF TOTAL LIME AND MAGNESIA**

**A-5.0** Lime and magnesia are determined as CaO and MgO. For this purpose, in a suitable aliquot (see A-4.2), containing not more than 20 mg of calcium, interfering elements are masked with sodium hydroxide-sodium cyanide solution and then calcium is titrated with standard EDTA (disodium salt) solution. Total calcium and magnesium are titrated in another equal aliquot with the same standard EDTA (disodium salt) solution and from the difference in the two titre values, magnesium is estimated.

### **A-5.1 Reagents**

**A-5.1.1** *Sodium Hydroxide Solution* — Approximately 2 N.

**A-5.1.2** *Sodium Hydroxide-Sodium Cyanide Solution* — Dissolve 1 g of sodium cyanide in 100 ml of 1 N sodium hydroxide.

**A-5.1.3** *Murexide Indicator* — Add 0.4 g of murexide (acid ammonium purpurate) to 40 g of sodium chloride and grind in a glass mortar to a homogeneous mixture.

**A-5.1.4** *Naphthol Green B Indicator* — 0.5 percent (m/v) solution in rectified spirit.

**A-5.1.5** *Eriochrome Black T Indicator* — Dissolve 0.5 g of the dye and 5 g of hydroxylamine hydrochloride in 100 ml of alcohol.

**A-5.1.6** *Ammonium Hydroxide Solution* — 1:3 (v/v).

**A-5.1.7** *Standard Calcium Solution* — 0.02 N. Weigh accurately 2.002 g of calcium carbonate, dried at 120°C, into a beaker and suspend in a little water. Cover the beaker in a watch glass and dissolve the material by slowly adding dilute hydrochloric acid. Wash down the sides of the beaker and the watch glass, transfer to a 1000 ml volumetric flask and make up the volume to the mark.

**A-5.1.8** *Standard EDTA Solution* — Dissolve about 7.5 g of EDTA (disodium salt) in 500 to 800 ml of water in a 1000 ml volumetric flask and dilute to the mark. Mix thoroughly and transfer to a polyethylene bottle.

**A-5.1.8.1** *Standardization* — Transfer 25 ml of the standard calcium solution to a 250-ml conical flask. Add 25 ml of water and then 2 N sodium hydroxide solutions in drops till the solution is just alkaline (indicated by a small piece of universal indicator paper). Add further 10 ml of 2 N sodium hydroxide solution in drops to bring the pH above 12. Add 50 mg of murexide indicator and 1 ml of naphthol green B indicator and titrate against EDTA solution until a distinct blue colour is obtained. From the titre value, calculate the molarity of the solution.

**A-5.1.9** *Buffer Solution (pH 10)* — Dissolve 68 g of ammonium chloride in 200 ml of water, add 570 ml of concentrated ammonia (relative density 0.91) and dilute to 1 litre.

### **A-5.2 Procedure**

**A-5.2.1** *Determination of Lime* — Pipette out 10 ml of the solution prepared in A-4.2 into a 250-ml conical flask. Add 50 ml of water and 2 N sodium hydroxide solutions in drops till the solution becomes just alkaline (indicated by a small piece of universal indicator paper).



Add further 10 ml of 2 N sodium hydroxide solutions in drops to bring the pH above 12. Add 10 ml of sodium hydroxide-sodium cyanide solution and mix well. Add 50 mg of murexide indicator and 1 ml of naphtholgreen B solution and titrate against standard EDTA (disodium salt) solution until a distinct blue colour is obtained.

#### **A-5.2.1.1 Calculation**

$$\text{Lime (as CaO), percent by mass} = \frac{5.608 \times V \times M}{m}$$

Where,

V = volume in ml of the standard EDTA solution used in titration,

M = molarity of EDTA solution, and

m = mass in grams of the material in the aliquot taken for the test.

**A-5.2.2 Determination of Magnesia** — Pipette out 10 ml of the solution prepared in A-4.2 into a beaker, add 50 ml of water and neutralize with ammonium hydroxide till the solution is slightly alkaline (tested by a small piece of universal indicator paper). Add 10 ml of buffer solution and a few drops of erichrome black T indicator solution to obtain a clear visible red colouration. Titrate the solution against standard EDTA (disodium salt) solution until a distinct blue colour is obtained.

$$\text{Magnesia (as MgO), percent by mass} = \frac{4.031 \times (V_1 - V) \times M}{m}$$

Where,

V<sub>1</sub> = volume in ml of EDTA solution used in titration,

V = volume in ml of EDTA solution used in titration in **A-5.2.1**,

M = molarity of EDTA solution, and

m = mass in g of the sample in the aliquot taken for the test.

**A-5.3 Total Lime and Magnesia** — Obtain total lime and magnesia (as CaO + MgO) by adding the values obtained in **A-5.2.1.1** and **A-5.2.2.1**.

### **A-6 DETERMINATION OF MOISTURE CONTENT**

**A-6.1 Procedure** — Weigh accurately about 50 g of the laboratory sample (*see* 5.1) in a suitable dish and dry at 105 to 110°C to a constant mass. Express the difference in mass as the percentage of mass of the material taken for the test.

### **A-7 DETERMINATION OF GRAIN SIZE DISTRIBUTION**

**A-7.1 Procedure** — Dry about 250 g of the laboratory sample (*see* 5.1) at 105 to 110°C, mix well and separate in two equal portions of 100 g each weighed accurately. Assemble 2.00-mm and 125-micron IS Sieves together with a receptacle and sieve the two portions separately. During sieving, shake the samples well for a period of at least 5 minutes with occasional tapping. Do not rub the sample over the screen. Weigh the material collected in the receptacle separately and calculate the respective percentages.

**A-7.2 Reporting the Result** — Report the average of the results of the two tests. To pass the test, material shall not be retained on 2.00-mm IS Sieve; nor that collected in the receptacle exceed 25 g.

## A-8 DETERMINATION OF SILICA

### A-8.1 Outline of the Method

The sample is brought to a solution after fusion with KOH and acidification with hydrochloric acid. SiO<sub>2</sub> as silicic acid thus formed reacts with excess potassium fluoride in a strongly acidic solution and potassium fluoride in a strongly acidic solution and potassium silicofluoride is precipitated. The filtered precipitate is allowed to hydrolyze in boiling water. The liberated hydrofluoric acid is titrated with a standard sodium hydroxide solution.

**TABLE 2 REQUIREMENTS FOR DOLOMITE FOR CERAMIC INDUSTRY**

(Clause 4.2)

SL. No.	CHARACTERISTICS	REQUIREMENT	METHOD OF TEST (REF TO CL NO. IN APPENDIX A)
(1)	(2)	(3)	(4)
i.	Moisture content, percent by mass, Max	2.0	A-6
ii.	Loss on ignition, percent by mass, <i>Max</i>	44	A-2
iii.	Silica (as SiO <sub>2</sub> ), percent by mass, <i>Max</i>	5.0	A-8
iv.	Iron oxide (as Fe <sub>2</sub> O <sub>3</sub> ), percent by mass, <i>Max</i>	0.5	A-9
v.	Calcium oxide (as CaO), percent by mass, <i>Min</i>	28	A-10
vi.	Magnesia (as MgO), percent by mass, <i>Min</i>	19	A-10

### A-8.2 Reagents

A-8.2.1 Potassium Chloride (Solid) — A. R. Grade.

A-8.2.2 Sodium Fluoride (Solid) — A.R. Grade.

A-8.2.3 Potassium Hydroxide (Solid) — A.R. Grade ( *see* IS 6031 ).

A-8.2.4 Sodium Hydroxide (Solid) — A. R. Grade.

A-8.2.5 Hydrochloric Acid — sp gr 1.18 ( *see* IS 265 ).

A-8.2.6 Nitric Acid — sp gr 1.42. ( *see* IS 264 ).

A-8.2.7 Bromothymol Blue — 0.5 percent (w/v) in absolute alcohol.

A-8.2.8 Potassium Hydrogenphthalate( Solid ) — A.R. Grade.

**A-8.2.9** *Standard NaOH Solution (N/15)*

Dissolve 5.575 g of NaOH in 200 ml of wafer (CO<sub>2</sub> free) in a polythene beaker and dilute to 2 litres. Store in a polythene bottle, Standardize the solution against potassium hydrogenphthalate using bromothymol blue as an indicator.

**A-8.2.10** Wash Solution

Dissolve 120 g of potassium chloride and 1 g of sodium fluoride in 1 litre of water. Add 4 to 5 drops of bromothymol blue indicator and add a few drops of HCl (1 : 4) to make the solution just yellow.

**A-8.3 Procedure**

**A-8.3.1** Place 10-12 pellets of KOH in a 25 ml capacity Nickel crucible and fuse it by placing the crucible on a burner. Place the crucible into a desiccator and cool to room temperature. Weigh 0.1-0.2 g of the dried (105-110°C) and powdered (200 mesh) sample and transfer into the nickel crucible containing fused KOH. Cover the crucible with lid and place it on a burner. Slowly raise the temperature of heating until fusion takes place. Keep the melt for 15 minutes with occasional swirling, cool and place the crucible in polythene beaker containing 30 ml of water. Add 25 ml of HNO<sub>3</sub> and 25 ml of HCl. After the melt is dissolved, remove the crucible and the lid and filter through rinsing with water. Dilute the solution with water to 100 ml. Add and dissolve 1 g of NaF in the solution by stirring with a polythene rod and then saturate the solution with KCl. The precipitation of K<sub>2</sub>SiF<sub>6</sub> is complete at this state. Allow the precipitate to settle. Filter the solution through No. 42 Whatman paper or its equivalent using a polythene funnel. Wash the beaker along the sides and transfer the washings and the precipitate on the filter paper. Wash the filter paper 4-5 times with the wash solution. Remove the filter paper with the contents and wash the outer surface with the wash solution and then transfer it to the polythene beaker with 25-30 ml of wash solution (kept on the ice-bath) and tear the filter paper to pieces with the help of the polythene rod. Wash down the inner surface of the beaker from the top with 10-15 ml of wash solution and place it again on the ice-bath. Neutralize the free mineral acid with standard N/15 NaOH solution at 10 ± 5°C to a blue end point using 3-4 drops of bromothymol blue indicator.

**A-8.3.2** In a separate step, boil 200 ml of water for 10 minutes in a 500 ml conical flask with 2-3 drops of HCl (1:4) and 5-6 drops of bromothymol blue. Neutralize the hot water with N/15 NaOH solution to just blue colour. Transfer 100 ml of this to a glass beaker and to the remaining hot water in the conical flask transfer the contents of the polythene beaker. Wash the polythene beaker for a few times with hot water kept in the glass beaker until the blue colour of water ceases to change. After transferring all washings to the conical flask, heat the flask to boiling and then titrate the liberated HF with standard N/15 NaOH. The end point is indicated by a change of colour from yellow to blue via green.

**A-8.3.3** Following the above procedure and carry out an experiment to obtain a blank value for the reagents only but without the sample.

### A-8.4 Calculation

$$\text{Percent SiO}_2 = \frac{N \times S \times 1.5013}{W}$$

Where,

N = volume of NaOH required for titration after deduction of the blank value,

S = strength of NaOH in normality, and

W = weight in g of the sample taken.

### A-9 DETERMINATION OF IRON

#### A-9.1 Outline of the Method

The sample is treated with HCl and water and any insoluble appearing is filtered and hydrofluorised in presence of a minimum of H<sub>2</sub>SO<sub>4</sub>. The residue remaining is fused with sodium carbonate and the melt dissolved in dil HCl is added to the main filtrate. Iron in the solution is determined with orthophenanthroline.

#### A-9.2 Preparation of Stock Solution

Weigh 1 g of dried (110°C) sample into a 250-ml beaker. Add 25 ml of water and 25 ml of hydrochloric acid. Cover the beaker with a watch glass and digest the sample on a hot plate until the reaction ceases. Evaporate the solution to dryness and bake it at 110°C. Next, add 20 ml of water and 10 ml of HCl and again digest on a hot plate. Filter the solution through a No. 40 Whatman paper or its equivalent and wash the residue several times with hot water. Ignite filter paper and digest the residue with hydrofluoric acid in a platinum crucible in the presence of 3-4 drops of sulphuric acid (1 : 1) and evaporate to dryness. Fuse the residue with sodium carbonate and dissolve the fused mass in hydrochloric acid (1 : 1), adding the solution to the main filtrate. Transfer the mixture into a 250-ml calibrated flask and dilute to volume.

#### A-9.3 Reagents

**A-9.3.1 Hydrochloric Acid** — sp gr 1.18, A. R. Grade.

**A-9.3.2 Hydrofluoric Acid** — 40 percent, A. R. Grade.

**A-9.3.3 Ammonia Solution** — sp gr 0.91, A. R. Grade.

**A-9.3.4 Sulphuric Acid** — sp gr 1.84, A. R. Grade.

**A-9.3.5 Sodium Carbonate (Solid)** — A. R. Grade.

**A-9.3.6 Hydroxylamine Hydrochloride** — A. R. Grade, 10 percent (w/v) in water.

**A-9.3.7 Tartaric Acid** — A. R. Grade, 10 percent (w/v) in water.

**A-9.3.8 Paranitrophenol** — 1 percent (w/v) alcoholic solution.

**A-9.3.9 Standard Iron Solution**

Dissolve 0.4911 g of ferrous ammonium sulphate  $\text{FeSO}_4 \cdot (\text{NH})_4\text{SO}_4 \cdot 6\text{H}_2\text{O}$  in water and add 10 ml of  $\text{H}_2\text{SO}_4$  (1:1) and 5 ml of hydrogen peroxide. Boil for 15 minutes to decompose the excess of  $\text{H}_2\text{O}_2$ . Cool and dilute to 1 litre in a calibrated flask (1 ml = 0.1 mg  $\text{Fe}_2\text{O}_3$ ).

#### **A-9.4 Procedure**

Transfer 5-20 ml of the solution (A-9.2) to a 100-ml calibrated flask. Add 1-2 drops of paranitrophenol indicator and 10 ml of tartaric acid solution. Neutralize the solution by dropwise addition of ammonia (1 : 3) to the yellow colour of the indicator. Acidify with a few drops of HCl (1 : 1). Add 2 ml of hydroxylammonium chloride and 10 ml of orthophenanthroline. Cool the solution in the flask and dilute to the mark. Measure the absorbance at 510 nm in a convenient cell against a reference test blank prepared in the same way but without the sample. Draw a calibration graph of concentration of  $\text{Fe}_2\text{O}_3$  against absorbance by taking 0, 1, 2, 3, 4 and 5 ml standard iron solution in 100-ml flask after developing a colour in the same way as in the test solution. Determine the iron ( $\text{Fe}_2\text{O}_3$ ) content with reference to the calibration graph.

#### **A-9.5 Calculation**

$$\text{Percent } \text{Fe}_2\text{O}_3 = \frac{A \times 1.25}{W}$$

Where,

A = mg of  $\text{Fe}_2\text{O}_3$  in test solution obtained from the calibration graph, and

W = weight in grams of the same taken. Test solution taken = 20 ml

### **A-10 DETERMINATION OF TOTAL CALCIUM OXIDE AND MAGNESIA**

#### **A-10.1 Reagents**

**A-10.1.1** *NaOH, solid*, A. R. Grade — Prepare 2 N.

**A-10.1.2** *Ammonium Chloride*, Solid, A. R. Grade

**A-10.1.3** *Ammonia-Ammonium Chloride Buffer* (pH 10)

Dissolve 67.59 g of ammonium chloride in 250 ml water, and 570 ml of ammonia solution and dilute to 1 litre with water.

**A-10.1.4** *Mixed Indicator*

Mix 0.08 g of naphthol green B, 0.05 g of O-Cresolphthalein complexone and 0.006 g of erichrome Black T with 20 g of ammonium chloride by grinding lightly in an agate mortar.

**A-10.1.5** *Calcium Chloride Solution* (0.025 M)

Dissolve 2.5 g of calcium carbonate ( $\text{CaCO}_3$ ) in the minimum amount of hydrochloric acid (1 : 1), boil off the carbon dioxide produced, transfer the solution into a 1-litre calibrated flask and dilute to the mark.

**A-10.1.6** *P and R Indicator*

**A-10.1.7 Triethanolamine (TEA)**

**A-10.1.8 Standard EDTA Solution (0.025 M)**

Dissolve 9.306 g of EDTA (disodium salt) in water, transfer the solution into 1 000 ml calibrated flask and dilute to the mark. Standardize the solution against calcium solution (**A-10.1.5**) according to the procedure **A-10.2.1** (for CaO only).

**A-10.2 Procedure**

**A-10.2.1** Transfer two 25-ml aliquots of the stock solution (A-10.2) separately to 250-ml conical flask. Dilute to 50-60 ml with water. Neutralize the solution in both the flasks with NaOH(2N) in presence of a very small universal indicator paper.

Acidify to pH 3-4 by drop wise addition of 30 percent HCl. Add 1 ml in excess. Mix the solution with 10 ml of 30 percent TEA solution thoroughly. Add 5 ml of Na<sub>2</sub>S solution (5% w/v).

**A-10.2.2** Add 10 ml of buffer (pH 10), about 0.2 g of mixed indicator to one of the flasks and titrate immediately with standard EDTA solution till the colour of the solution changes from pink to green.

**A-10.2.3** Add to the other flask 5 ml of NaOH(5N) and dilute to about 100 ml. Add 0.2 g of P & R indicator and immediately titrate with EDTA till the colour of the solution changes from pink to blue.

**A-10.3 Calculation**

$$\text{Percent CaO} = \frac{BX \times 100}{W}$$
$$\text{Percent MgO} = \frac{(A - B)Y \times 100}{W}$$

Where,

A = volume in ml of EDTA solution used in titration (**A-10.2.2**),

B = volume in ml of the EDTA solution used in titration (**A-10.2.3**),

X = equivalent CaO g/ml of EDTA,

Y = equivalent MgO g/ml, and

W = weight of the sample in the 50-ml aliquot.