BRITISH STANDARD

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Specification for

Limestone for making colourless glasses

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Cooperating organizations

The Laboratory Apparatus Standards Committee, under whose direction this British Standard was prepared, consists of representatives from the following Government departments and scientific and industrial organizations:

Agricultural Research Council
Association for Science Education
British Educational Equipment Association
British Laboratory Ware Association
British Lampblown Scientific Glassware Manufacturers' Association Ltd.
British Pharmacopoeia Commission
Chemical Industries Association
Chemical Society
Chemical Society, Analytical Division
Department of Health and Social Security
Department of Industry (Laboratory of the Government Chemist)
Glass Manufacturers' Federation
Institute of Petroleum
Ministry of Defence
Pharmaceutical Society of Great Britain
Scientific Instrument Manufacturers' Association
Society of Chemical Industry
Society of Glass Technology*
Standardization of Tar Products Tests Committee

The organization marked with an asterisk in the above list was directly represented on the committee entrusted with the preparation of this British Standard.

This British Standard, having been prepared under the direction of the Laboratory Apparatus Standards Committee, was published under the authority of the Executive Board and comes into effect on 30 September 1980

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Contents

Foreword

This British Standard has been prepared under the direction of the laboratory Apparatus Standards Committee in close cooperation with the Society of Glass Technology (SGT). The Society of Glass Technology has been concerned for many years with the standardization of the methods of chemical analysis of glass and of the raw materials and refractories used in its manufacture. The Society published a specification for limestone for making colourless glasses in 1937[1], and revisions of the specification appeared in 1943[2], 1956[3] and 1972[4]. The 1956 revision was used as the basis of the first edition of this British Standard, published in 1959, and the 1972 revision was used as the basis for the present British Standard. This British Standard supersedes BS 3108:1959, which is therefore withdrawn.

The SGT specification includes general recommendations for the inspection of a sample of the limestone for obvious impurities such as magnetic materials or unusual mineral formations. No limits are specified for these items and they have therefore not been included as a mandatory part of the present standard; nevertheless, for the information of users, the inspection methods recommended by the SGT are given in Appendix A.

Certain requirements for the composition of the limestone are not specified in this standard and are subject to agreement between purchaser and supplier; recommended agreements between purchaser and supplier for these requirements and recommended declarations by the supplier are given in Appendix D.

Summary of pages

This document comprises a front cover, an inside front cover, pages i and ii, pages 1 to 8, an inside back cover and a back cover.

This standard has been updated (see copyright date) and may have had amendments incorporated. This will be indicated in the amendment table on the inside front cover.

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[1] *J.Soc. Glass Tech.,* **21** (1937), 111 – 119.
[2] *ibid,* **29** (1943), 140 – 149.
[3] *ibid,* **40** (1956), 130 – 139.
[4] *Glass Technology,* **13** (1972), 104 – 109.

1 Scope

This British Standard specifies the essential requirements and methods of test for limestone for making colourless glasses, i.e. glass that has no appreciable tint when viewed through the thickness normally encountered in practice.

2 References

The titles of the publications referred to in this standard are listed on the inside back cover.

3 Sampling

A representative sample of the material shall be obtained for each test by the appropriate method specified in Appendix B.

4 Chemical composition

The chemical composition of the sample when analysed by the methods specified in Appendix C shall comply with the following requirements.

a) The calcium content, expressed as calcium oxide (CaO), shall be not less than 55.2 %.

NOTE This is equivalent to a calcium carbonate content of 98.5 %.

b) The total iron content, expressed as ferric oxide (Fe_2O_3), shall not exceed 0.035 %.

c) The total non-volatile matter insoluble in hydrochloric acid shall not exceed 1.0 %.

d) The organic matter shall not exceed 0.1 %.

e) Colouring elements, other than iron, shall not be present to an extent sufficient to produce a colour in the glass.

Appendix A Method of inspection for contamination

A.1 Magnetic materials

Dry, at a temperature of 100 °C, approximately 100 g of the 500 g sample prepared as described in **B.2.1** and test with a magnet. Examine microscopically any magnetic material found, in order to differentiate between naturally occurring minerals and particles of metallic iron or scale acquired during crushing, handling or transport.

A.2 Carbonaceous matter

Dry, at a temperature of 110 °C, the remainder of the 500 g sample and inspect for unusual mineral formations and peaty or carbonaceous matter. Confirm the presence of any of these by microscopic examination.

Appendix B Methods of sampling

B.1 Sampling from bulk

Take a representative sample of the bulk by a method previously agreed upon by the purchaser and supplier.

NOTE The recommended method is as follows.

a) Collect a total mass of sample equal to 0.25 kg per 1 000 kg of the bulk, taking separate and approximately equal portions from at least 12 different places in the bulk; four from the top, four from the centre, and four from the bottom.

b) Immediately mix thoroughly these separate portions constituting the sample, and pack immediately into containers[5] so that the original condition is preserved until the sample is required for test.

c) Ensure that the total mass of the sample is not less than 2 kg, and in the event of the bulk exceeding 10 000 kg, take a correspondingly large sample and reduce to a convenient size (2 kg) by an approved method agreed upon by purchaser and supplier.

B.2 Sampling for tests

Mix the contents of the containers holding the representative sample of the bulk and then spread the contents out in a layer and take the following samples.

NOTE Sampling should be carried out with the aid of a thin-bladed spatula to avoid segregation of different particle sizes.

B.2.1 *Sample for inspection for contamination.* Take at least 20 separate and approximately equal portions from different places to yield a total mass of approximately 500 g. The recommended method of inspection for contamination is given in Appendix A.

B.2.2 *Laboratory sample.* Reduce the remainder of the representative sample (**B.2**) by mixing and quartering or with the aid of a sample divider, until a sample of approximately 1 kg is obtained. Spread this sample out in a layer and then take the following samples.

B.2.2.1 *Sample for moisture determination.* Take at least ten separate and approximately equal portions from different parts to yield a total mass of approximately 50 g. Immediately determine the moisture content of this sample in accordance with the method specified in Appendix E.

B.2.2.2 *Sample for chemical analysis.* Take at least ten separate and approximately equal portions from different parts to yield a total mass of approximately 50 g. Analyse this sample in accordance with the methods specified in Appendix C.

B.2.2.3 *Sample for size grading test.* Take approximately equal portions from different parts to yield a total mass of at least 500 g. Test this sample for size grading in accordance with the method specified in Appendix F.

Appendix C Methods for the determination of chemical composition

C.1 General

The constituents to be determined in the analysis of a limestone to be used for making colourless glasses are non-volatile matter including silica, aluminium oxide, total calcium expressed as calcium oxide, magnesium oxide, total iron expressed as ferric oxide, and organic matter.

C.2 Reagents

The following reagents are required.

NOTE 1 All reagents used should be free from such amounts of impurities as might endanger the accuracy of the determinations in question; analytical reagent quality will normally be suitable but provision should be made for blank determinations where these are considered to be essential. Water complying with the requirements of BS 3978 should be used throughout.

NOTE 2 The following designation is used for the solutions of acids and of ammonia. Concentrated reagents are specified, where necessary, in terms of percentage and the approximate normality in brackets. The diluted reagents are specified by giving the proportions by volume in which the appropriate concentrated reagent is to be diluted with water. Concentrated hydrochloric acid is described as hydrochloric acid 36 % *m*/*m* (11N) and hydrochloric acid 1 + 4 refers to the solution obtained by diluting one volume of hydrochloric acid 36 % *m*/*m* (11N) with four volumes of water. Solutions are aqueous unless otherwise stated.

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[5] Sealed plastics bags or glass jars fitted with non-metallic caps are suitable. If no determination of moisture is to be made, stout linen bags may be used.

C.2.1 *4-Nitrophenol indicator solution,* 1 g/l.

C.2.2 *Calcium carbonate,* dried at a temperature of 110 °C for 2 h and stored in a stoppered weighing bottle.

C.2.3 *Sodium carbonate,* anhydrous.

C.2.4 *Chloroform,* B.P. grade.

C.2.5 *Ethanol,* 95 % *V/V.*

C.2.6 *Ammonia solution,* concentrated, 35 % *m/m* (18N).

C.2.7 *Ammonia solution,* diluted 1 + 1.

C.2.8 *Ammonia solution,* diluted 1 + 3.

C.2.9 *Ammonium acetate buffer solution.* Add, with stirring, 120 ml of glacial acetic acid to 500 ml of water, followed by 84 ml of ammonia solution (**C.2.6**). Cool, dilute to 1 litre and mix.

C.2.10 *Ammonium chloride/ammonia buffer solution.* Make up the following two solutions:

Solution 1	Add 67.5 g of ammonium chloride to 570 ml of the concentrated ammonia solution (**C.2.6**) and dilute to 950 ml with water.
Solution 2	Dissolve 0.616 g of magnesium sulphate ($MgSO_4.7H_2O$) in 50 ml of water, add 0.93 g of ethylenediamine-*NNN′N′*-tetra-acetic acid disodium salt dihydrate (EDTA) and stir to dissolve.

Mix solutions 1 and 2.

C.2.11 *Ammonium molybdate solution,* 80 g/l. Dissolve 80 g of ammonium molybdate [$(NH_4)_6 Mo_7O_{24}.4H_2O$] in water, filter if necessary, and dilute to 1 litre. Store in a polyethylene bottle. Discard after 4 weeks, or earlier if any appreciable deposit is observed.

C.2.12 *Ammonium nitrate solution,* 20 g/l. Dissolve 20 g of ammonium nitrate in 1 litre of water, add a few drops of methyl red indicator (**C.2.42**) and add 1 + 1 ammonia solution (**C.2.7**) until the indicator just turns yellow.

C.2.13 *Bromine water,* saturated solution.

C.2.14 *Calcium solution.* Dissolve 10 g of calcium carbonate in 50 ml of the 1 + 1 hydrochloric acid (**C.2.17**), boil to eliminate CO_2, cool and dilute with water to 1 litre.

NOTE 50 ml of calcium solution ≡ 0.5 g $CaCO_3$.

C.2.15 *Cupferron solution,* 60 g/l. Dissolve 1.5 g of cupferron (see note) in 25 ml of water and filter if necessary. This solution shall be freshly prepared.

NOTE If the reagent is discoloured or gives a strongly coloured solution a new stock should be obtained. The solid reagent should be stored in a tightly stoppered bottle in the presence of a piece or pieces of ammonium carbonate to prevent decomposition.

C.2.16 *Hydrochloric acid solution,* concentrated, 36 % *m/m* (11N).

C.2.17 *Hydrochloric acid solution,* diluted 1 + 1.

C.2.18 *Hydrochloric acid solution,* diluted 1 + 4.

C.2.19 *Hydrochloric acid solution,* N.

C.2.20 *Hydrofluoric acid solution,* 40 % *m/m.*

C.2.21 *Hydroxylammonium chloride solution,* 200 g/l.

C.2.22 *Nitric acid solution,* concentrated, 70 % *m/m* (16N).

C.2.23 *1,10-Phenanthroline hydrate solution,* 1 g/l. Dissolve 1 g of the solid in the minimum volume of the 1 + 1 hydrochloric acid (**C.2.17**) and dilute with water to 1 litre.

C.2.24 *Sodium acetate buffer solution.* Dissolve 54 g of hydrated sodium acetate in water, add 93 ml of glacial acetic acid and dilute to 1 litre.

C.2.25 *Sodium hydroxide solution,* 5N.

C.2.26 *Sodium hydroxide solution,* N.

C.2.27 *Sodium sulphate solution,* 150 g/l.

C.2.28 *Sodium sulphate/ethanol wash solution.* Dilute 10 ml of the sodium sulphate solution (**C.2.27**) to 90 ml with water, add 10 ml of ethanol and mix.

C.2.29 *Sulphuric acid solution,* diluted 1 + 1. Add 500 ml of sulphuric acid, concentrated 98 % *m/m* (36N), to 500 ml of water, slowly, carefully and with stirring; much heat is evolved.

C.2.30 *Triethanolamine solution,* diluted 3 + 7.

C.2.31 *Ethylenediamine-NNN′N′-tetra-acetic acid disodium salt dihydrate (EDTA),* 50 g/l standard solution. Dissolve 50 g of EDTA in 1 litre of water, allow to stand overnight, and filter if necessary. Standardize as follows.

> Weigh out accurately, to the nearest 0.0002 g, approximately 0.5 g of calcium carbonate, dissolve in 5 ml of the 1 + 4 hydrochloric acid (**C.2.18**), dilute with water to about 50 ml, boil for a few minutes, and cool. Add 10 ml of triethanolamine (**C.2.30**), 5 ml of the 5N sodium hydroxide solution (**C.2.25**), 0.2 g of HSN indicator mixture (**C.2.41**) and titrate immediately with the EDTA solution to the blue end-point.

C.2.32 *Ethylenediamine-NNN′N′-tetra-acetic acid disodium salt dihydrate (EDTA),* 0.05M. Dissolve 18.613 g of EDTA in water, filter if necessary and dilute to 1 litre. Standardize as follows.

a) Wash zinc metal in N hydrochloric acid (**C.2.19**) to remove any oxide film, then wash successively with water, ethanol and ether. Dissolve 3.2685 g of the oxide-free zinc in 100 ml of the N hydrochloric acid (**C.2.19**); cover the beaker with a watch glass and allow to stand overnight on a steam bath. Cool, dilute with water to 1 litre and mix. 1 ml of this solution is equivalent to 2.55 mg of Al_2O_3.

b) Transfer 50.0 ml of the EDTA solution to a 500 ml conical flask and add five drops of concentrated hydrochloric acid (**C.2.16**). Add a few drops of the bromophenol blue solution (**C.2.38**) and then add ammonium acetate buffer solution (**C.2.24**) until the indicator turns blue, followed by 10 ml in excess.

Add a volume of ethanol equal to the total volume of the solution, followed by 1 ml to 2 ml of dithizone indicator solution (**C.2.40**) and titrate with the standard zinc solution until the blue colour changes to the first appearance of a permanent pink colour. From the titration calculate the factor for 1 ml of EDTA in terms of Al_2O_3.

C.2.33 *Ethylenediamine-NNN′N′-tetra-acetic acid disodium salt dihydrate (EDTA),* 0.01M. Dissolve 3.722 g of EDTA in water and dilute to 1 litre. Standardize as follows.

Transfer 25.0 ml of magnesium standard solution (**C.2.36**) to a 250 ml conical flask, add 10 ml of ammonium chloride/ammonia buffer solution (**C.2.10**) and a few drops of mordant black 11 indicator solution (**C.2.43**). Titrate with EDTA solution until the colour of the solution changes from bluish red to blue, the end-point being that at which the last trace of red disappears.

C.2.34 *Iron standard solution,* containing the equivalent of 0.1 g of ferric oxide (Fe_2O_3) per litre. Dissolve 0.4911 g of ammonium ferrous sulphate [$(NH_4)_2SO_4.FeSO_4.6H_2O$] in water, adding 10 ml of the concentrated hydrochloric acid solution (**C.2.16**), and dilute to 1 litre.

C.2.35 *Iron standard solution,* containing the equivalent of 10 μg of ferric oxide (Fe_2O_3) per millilitre, prepared immediately before use by diluting 10 ml of iron standard solution (**C.2.34**) to 100 ml.

C.2.36 *Magnesium standard solution.* Dissolve 0.2432 g of pure magnesium metal in 20 ml of the 1 + 4 hydrochloric acid (**C.2.18**) and dilute with water to 1 litre.

NOTE 1 ml of this solution ≡ 0.403 mg MgO.

C.2.37 *Silica standard solution.* Fuse 0.100 g of silica (not less than 99.8 % SiO_2) with 2.0 g of anhydrous sodium carbonate in a platinum crucible. Dissolve the cold melt in water and dilute to 1 litre. Transfer immediately to a polyethylene bottle.

C.2.38 *Bromophenol blue indicator solution,* 0.4 g/l.

C.2.39 *Di(2-hydroxyphenylimino)-ethane indicator solution.* Dissolve 0.03 g of the solid in 100 ml of ethanol or industrial methylated spirit.

NOTE Di(2-hydroxyphenylimino)-ethane is also known as glyoxal-bis(2-hydroxy-anil).

C.2.40 *Dithizone indicator solution,* 0.25 g/l. Dissolve 0.0125 g of dithizone in 50 ml of ethanol (**C.2.5**). This solution will keep for about 1 week.

C.2.41 *HSN indicator mixture.* Intimately mix, by grinding, 0.05 g of 2-hydroxy-1-(2-hydroxy-4-sulpho-1-naphthylazo)-3-naphthoic acid with 25 g of sodium chloride.

C.2.42 *Methyl red indicator solution,* 0.1 g/l.

C.2.43 *Mordant black 11 indicator solution.* Dissolve 1 g of solochrome black (C.I.14645) in 100 ml of triethanolamine (**C.2.30**). This solution is stable for at least 6 months.

C.3 Preparation of the sample

Roughly grind the sample taken for chemical analysis (**B.2.2.2**) in an agate mortar, spread out in a layer and take portions from different parts to yield a sample of approximately 20 g. Grind this sample finely, dry at a temperature of 110 °C for 2 h and transfer to a stoppered weighing bottle. Store in a desiccator. Transfer the remainder of the roughly ground sample to a second weighing bottle.

C.4 Qualitative analysis

Carry out a qualitative analysis to establish whether impurities such as chromium, manganese, lead, sulphur or phosphorus are present in more than trace amounts. Examination of the residue, after treatment of approximately 5 g of the roughly ground sample (**C.3**) with the 1 + 1 hydrochloric acid (**C.2.17**), will reveal the presence of carbonaceous matter. Any oily matter will show as drops or as a scum adhering to the beaker wall.

C.5 Preparation of solutions for analysis and gravimetric determination of acid-insoluble silica

Weigh, to the nearest 0.001 g, approximately 5 g of the prepared sample (**C.3**), transfer to a beaker and dissolve in 50 ml of the 1 + 1 hydrochloric acid (**C.2.17**). Boil gently to ensure solution of soluble matter, then filter off any residue on a medium filter paper, and wash well with hot water. Reserve the filtrate (solution A). The residue on the filter paper is required for the determination of the acid-insoluble silica.

Prepare a blank solution by transferring 20 ml of the 1 + 1 hydrochloric acid (**C.2.17**) to a beaker and evaporating to dryness. Dissolve the residue in 30 ml of the 1 + 1 hydrochloric acid (**C.2.17**), then filter off any residue on a medium filter paper and wash well with hot water. Reserve the filtrate (solution B). Treat the paper as described below.

Place the paper containing the insoluble matter in a weighed platinum crucible. Partially cover with a lid and heat gently until the carbon has been oxidized. Cover the crucible, ignite at a temperature of 1 200 °C for 15 min, cool in a desiccator and weigh. Repeat the ignition until constant mass (m_1) is attained.

Moisten the ignited residue with water, add 5 ml of hydrofluoric acid (**C.2.20**) and three drops of sulphuric acid (**C.2.29**). Evaporate the more volatile constituents, drive off the sulphuric acid by heating the crucible on a hot-plate, then cautiously heat the crucible over a free flame. Finally cover with the lid and ignite at a temperature of 1 200 °C for 2 min. Cool in a desiccator and weigh the crucible and lid (mass m_2).

From the mass of silica found ($m_1 - m_2$) calculate the percentage of silica insoluble in hydrochloric acid that is present in the residue.

Fuse the residue from the hydrofluoric acid treatment with 1 g of anhydrous sodium carbonate (**C.2.3**), extract the cold mass with 5 ml of the 1 + 1 hydrochloric acid (**C.2.17**) and add the clear solution to solution A. Transfer the cold filtrate to a 500 ml one-mark volumetric flask, dilute to the mark with water and mix (solution C).

C.6 Spectrophotometric determination of soluble silica

Transfer 50 ml aliquot portions of solution C into two separate 100 ml one-mark volumetric flasks. Add two drops of 4-nitrophenol indicator solution (**C.2.1**) and then add the 1 + 1 ammonia solution (**C.2.7**) until the deep yellow colour just appears. Immediately add 10 ml of the 1 + 4 hydrochloric acid solution (**C.2.18**) to each flask, and to only one flask 10 ml of ammonium molybdate solution (**C.2.11**). Dilute each to the mark and mix. Allow the solutions to stand for 5 min and then measure the absorbance of the molybdate-containing solution at a wavelength of 420 nm in a 40 mm cell using the molybdate-free solution as a reference; complete the measurement within 15 min of adding the molybdate solution. Determine the colorimetric blank of the ammonium molybdate solution (**C.2.11**) by adding 10 ml of 1 + 4 hydrochloric acid (**C.2.18**) to a 100 ml one-mark volumetric flask containing 50 ml of water, followed by 10 ml of ammonium molybdate solution (**C.2.11**), diluting to the mark and mixing. Measure as described above but using water as the reference solution.

Subtract the colorimetric blank of the ammonium molybdate solution from the absorbance reading of the sample and calculate the soluble silica from a calibration graph relating mass of silica to absorbance. From the mass of silica found calculate the percentage and add it to the percentage found for the acid-insoluble silica to give the total percentage of silica in the limestone.

Prepare a calibration graph as follows.

a) Transfer measured volumes of the standard silica solution (**C.2.37**), covering the range 0 ml to 12 ml, to separate 100 ml one-mark volumetric flasks. Add to each flask 50 ml of the calcium solution (**C.2.14**) and dilute, if necessary, to about 60 ml. Add 10 ml of the 1 + 4 hydrochloric acid (**C.2.18**) and 10 ml of ammonium molybdate solution (**C.2.11**), dilute to the mark with water and mix.

b) Allow the solutions to stand for 5 min and then measure the absorbance of the solutions at a wavelength of 420 nm using 40 mm cells, with water as reference; complete the measurement within 15 min from the addition of the ammonium molybdate solution. Plot the difference between the absorbances of the solutions and the blank against the corresponding masses of silica, to give a calibration graph.

C.7 Gravimetric determination of alumina

C.7.1 *Separation of "R_2O_3".* Transfer 200 ml of solution C (see **C.5**) to a 400 ml beaker, add five drops of nitric acid (**C.2.22**) and boil for 15 min. Add 5 ml of concentrated hydrochloric acid (**C.2.16**) and when near to boiling add 1 + 1 ammonia solution (**C.2.7**) drop by drop, with stirring, until the solution is almost neutral, then add three drops of methyl red indicator solution (**C.2.42**). Continue the addition of 1 + 1 ammonia solution (**C.2.7**) drop by drop, with stirring, until the indicator just turns yellow. Boil for 1 min, then keep almost at boiling-point for 10 min, maintaining the faintly ammoniacal condition.

C.7.2 *Gravimetric determination of "R_2O_3".* Filter off the precipitate obtained as described in **C.7.1** on a 90 mm medium filter paper and wash the precipitate three times with hot ammonium nitrate solution (**C.2.12**). Discard the filtrate.

Dissolve the precipitate in hot 1 + 1 hydrochloric acid (**C.2.17**), collecting the solution in the original beaker, and reprecipitate the hydroxides with 1 + 1 ammonia solution (**C.2.7**) as described above. Filter off the precipitate on a medium filter paper, and wash with hot ammonium nitrate solution (**C.2.12**) until free from chloride.

Transfer the precipitate and paper to an ignited weighed platinum crucible, and heat gently until the carbon has been oxidized. Cover the crucible, ignite it at a temperature of 1 200 °C for 5 min, allow the crucible and contents to cool, add 5 ml of hydrofluoric acid (**C.2.20**) and six drops of the sulphuric acid (**C.2.29**) to the residue. Digest the mixture on a steam-bath, then evaporate to dryness cautiously, avoiding spurting. Cover the crucible, ignite it at a temperature of 1 200 °C for 5 min, allow the crucible and contents to cool in a desiccator and weigh.

Repeat the process of igniting, cooling and weighing until constant mass is attained.

C.7.3 *Calculation of alumina.* From the mass of "R_2O_3" obtained, calculate the percentage in the sample. Subtract the ferric oxide (Fe_2O_3) content (see **C.11**) and report the difference as the percentage of alumina (Al_2O_3).

C.8 Alternative volumetric determination of alumina

C.8.1 *Separation of "R_2O_3".* Filter off the precipitate obtained as described in **C.7.1** on a 90 mm hardened medium filter paper, rinse the beaker with hot ammonium nitrate solution (**C.2.12**). Discard the filtrate and then wash the precipitate through the filter with 40 ml of the 1 + 1 hydrochloric acid (**C.2.17**). Wash the paper thoroughly with hot water and discard the paper.

C.8.2 *Separation of iron and titanium.* Cool the solution and transfer it to a separating funnel. The volume at this stage should be about 100 ml.
Add 20 ml of chloroform (**C.2.4**) and 10 ml of cupferron solution (**C.2.15**). Stopper the funnel and shake vigorously. Release the pressure in the funnel by carefully removing the stopper and rinse the stopper and neck of the funnel with water. Allow the layers to separate and withdraw the chloroform layer. Confirm that extraction is complete by checking that the addition of a few drops of cupferron solution (**C.2.15**) does not produce a permanent coloured precipitate. Add 10 ml portions of chloroform (**C.2.4**) and repeat the extraction until the chloroform layer is colourless. Use a polyethylene wash bottle containing chloroform to wash the stem of the funnel, both inside and out.

C.8.3 *Volumetric determination of alumina.* Discard the chloroform extracts and transfer the aqueous solution to a 500 ml conical flask. Add a few drops of bromophenol blue indicator solution (**C.2.38**) and then add concentrated ammonia solution (**C.2.6**) drop by drop, until the solution is just alkaline. Reacidify quickly with concentrated hydrochloric acid (**C.2.16**) and add five drops in excess.
Add 10.0 ml of standard EDTA solution (**C.2.32**) and add ammonium acetate buffer solution (**C.2.9**) until the indicator turns blue, followed by 10 ml in excess. Boil the solution for 10 min and cool. Add a volume of ethanol (**C.2.5**) equal to the total volume of the solution, followed by 1 ml to 2 ml of dithizone solution (**C.2.40**).

Titrate the excess EDTA, using a semi-micro or similar burette, with the standard zinc solution [see **C.2.32** a)] until the blue colour changes to the first appearance of a permanent pink colour.
Calculate and report the percentage of alumina (Al_2O_3) of the sample from the volume of EDTA complexed with alumina.

C.9 Determination of calcium oxide

Transfer 50 ml of solution C (see **C.5**) to a 250 ml conical flask. Add 10 ml of triethanolamine solution (**C.2.30**) and 5 ml of 5N sodium hydroxide solution (**C.2.25**). Add 0.15 g of HSN indicator mixture (**C.2.41**) and titrate immediately with standard EDTA solution (**C.2.31**), the end-point being marked by a colour change from red through purple to pure blue.

Report the percentage of calcium oxide in the sample.

C.10 Determination of magnesium oxide

Transfer 100 ml of solution C (see **C.5**) to a 250 ml beaker. Add three drops of methyl red indicator (**C.2.42**) and titrate the excess acid with N sodium hydroxide (**C.2.26**) to the neutral point of the indicator. To the neutral solution add 2.0 ml of N hydrochloric acid (**C.2.19**) and boil the solution until the volume is reduced to about 30 ml. Remove the beaker from the source of heat and carefully add 0.2 g of calcium carbonate (**C.2.2**) followed by five drops of bromine water (**C.2.13**). Heat the solution and boil for 15 s. Remove the beaker from the burner and while stirring add 25 ml of sodium sulphate solution (**C.2.27**). Add 10 ml of ethanol (**C.2.5**) and again stir. Filter the solution through a sintered glass crucible of porosity grade 4, collecting the filtrate in a beaker. Transfer as much of the precipitate as possible to the crucible without any washing and apply a good suction. Add 5 ml of the sodium sulphate/ethanol wash solution (**C.2.28**) to rinse the beaker and immediately transfer the rinsings to the crucible with the vacuum already applied. Repeat the rinsing twice more with two further 5 ml portions of the wash solution, sucking dry between each rinse. Remove the crucible and rinse the underside with distilled water, collecting the rinsings in the beaker containing the filtrate. Transfer the filtrate and washings to a 250 ml one-mark volumetric flask and dilute to the mark with water. Mix thoroughly.

Titrate any residual calcium as follows. Pipette 100 ml of the solution into a 400 ml beaker, add 100 ml of water, 5 ml of triethanolamine solution (**C.2.30**) and 2 ml of 5N sodium hydroxide solution (**C.2.25**) and mix well. Stand the beaker against a white background, add 7 ml of di-(2-hydroxyphenylimino)-ethane indicator solution (**C.2.39**), and stir for 1 min. Immediately titrate the solution with standard EDTA solution (**C.2.33**) until the colour changes from orange red to lemon yellow. It is essential that this titration is accurate, but the volume of EDTA need not be noted.

Add a small piece of litmus paper to the titrated solution and neutralize with N hydrochloric acid (**C.2.19**). This decolourises the solution. Add 2 ml of N hydrochloric acid (**C.2.19**) and stir to dissolve the magnesium hydroxide. Neutralize the solution by addition of the 1 + 1 ammonia solution (**C.2.7**), remove the litmus paper and add 5 ml of ammonium chloride/ammonia buffer solution (**C.2.10**), followed by a few drops of mordant black 11 indicator solution (**C.2.43**). Titrate with EDTA (**C.2.33**) until the colour of the solution changes from bluish red to blue, the end-point being the point at which the last trace of red disappears. Calculate and report the percentage of magnesium oxide in the sample.

C.11 Determination of total iron content

(expressed as Fe_2O_3).Transfer 25 ml portions of solutions B and C to separate 100 ml one-mark volumetric flasks and to each flask add 2 ml of hydroxylammonium chloride solution (**C.2.21**) and two drops of 4-nitrophenol indicator solution (**C.2.1**). Add the 1 + 3 ammonia solution (**C.2.8**) until the solution just changes to a deep yellow colour. Add the 1 + 4 hydrochloric acid (**C.2.18**) drop by drop until the solution becomes colourless[6], then add 10 ml of 1,10-phenanthroline solution (**C.2.23**). Add 10 ml of sodium acetate buffer solution (**C.2.24**), dilute to the mark with water and mix thoroughly. Measure the absorbance of the solution after 15 min using a 40 mm cell at a wavelength of 510 nm against the blank solution as reference and use the calibration graph to calculate the mass of ferric oxide. Report the percentage of iron, expressed as ferric oxide (Fe_2O_3), in the sample.

Prepare a calibration graph as follows. Transfer aliquot portions of standard iron solution containing from 0 µg to 90 µg of ferric oxide to separate 100 ml one-mark volumetric flasks and add 25 ml of calcium solution (**C.2.14**) to each flask. Add 2 ml of hydroxylammonium chloride solution (**C.2.21**) and two drops of 4-nitrophenol indicator solution (**C.2.1**). Add the 1 + 3 ammonia solution (**C.2.8**) until the solution just changes to a deep yellow colour. Add the 1 + 4 hydrochloric acid (**C.2.18**) drop by drop until the solution becomes colourless, then add 10 ml of 1,10-phenanthroline solution (**C.2.23**). Add 10 ml of sodium acetate buffer solution (**C.2.24**) and dilute to the mark with water and mix thoroughly. Measure the absorbance of the solution after 15 min using 40 mm cells at a wavelength of 510 nm against the solution containing no iron. Plot the absorbance readings against mass of ferric oxide to give a calibration graph.

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[6] With high iron contents the solution may remain pale yellow. In this case add hydrochloric acid until the first sharp change in colour takes place, from deep yellow to pale yellow.

C.12 Direct determination of calcium oxide

Weigh, to the nearest 0.002 g, approximately 2.5 g of the sample (**B.2.2.2**) and transfer to a 400 ml beaker. Dissolve in 50 ml of the 1 + 4 hydrochloric acid (**C.2.18**) and boil gently for 10 min. Filter the solution through a 90 mm medium filter paper, wash the beaker and paper thoroughly with hot water. Cool and dilute the cold filtrate to a volume of 250 ml in a one-mark volumetric flask and mix.

Transfer a 50 ml aliquot portion into a 250 ml conical flask and complete the determination as described in **C.9**.

C.13 Determination of organic matter

Dry the remainder of the roughly ground sample (**C.3**) at a temperature of 110 °C, cool and weigh out a mass of 10 g. Dissolve in excess of the 1 + 1 hydrochloric acid (**C.2.17**), filter off the insoluble matter on a porous porcelain crucible, wash well with hot water, then dry at a temperature of 110 °C, cool and weigh. Ignite at a temperature of 900 °C for 15 min, cool and weigh. From the loss in mass, calculate and report the percentage of organic matter in the sample.

Appendix D Recommendations for the requirements to be agreed between the purchaser and the supplier and recommended declarations to be made by the supplier

D.1 Moisture content

The maximum acceptable moisture content of the limestone as received should be the subject of agreement between purchaser and supplier, but should normally not be greater than 2 % when determined by the method specified in Appendix E.

D.2 Size grading

The percentages of grains of different sizes constituting the sample should be agreed between purchaser and supplier. Recommended specifications are as follows, using sieves complying with the requirements of BS 410 and the method specified in Appendix F.

a) *Limestone for use in tank furnaces*

Nominal aperture of sieve	Residue retained by sieve
mm	%
4.75	0
3.35	≯1

b) *Limestone for use in pot furnaces*

Nominal aperture of sieve	Residue retained by sieve
mm	%
3.35	0
1.00	≯5

D.3 Alumina and magnesia

Any limiting value for alumina (Al_2O_3) and magnesia (MgO) should be the subject of agreement between purchaser and supplier.

D.4 Chemical composition: declaration by the supplier

If other impurities such as manganese, lead, sulphur and phosphorus are present to the extent of 0.1 % individually, when expressed as oxide, their presence and amount should be declared by the supplier.

Appendix E Determination of moisture content

Weigh the sample reserved for moisture determination, obtained as described in **B.2.2.1**, into a suitable dish and dry at a temperature of 100 °C until constant mass is attained. Calculate the loss in mass as a percentage of the original mass, and report as moisture content.

Appendix F Determination of size grading (sieve analysis)

F.1 General

In this determination of size grading, use sieves complying with the requirements of BS 410.

F.2 Limestone for use in tank furnaces

Weigh 500 g of the sample (see **B.2.2.3**) and sift through a sieve of nominal aperture 4.75 mm and then through a sieve of nominal aperture 3.35 mm, in portions of approximately 100 g. Weigh the quantity of limestone remaining on each sieve and calculate and report as a percentage.

F.3 Limestone for use in pot furnaces

Weigh 500 g of the sample (see **B.2.2.3**) and sift through a sieve of nominal aperture 3.35 mm and then through a sieve of nominal aperture 1.00 mm, in portions of approximately 100 g. Weigh the quantity of limestone remaining on each sieve and calculate and report as a percentage.

Publications referred to

BS 410, *Specification for test sieves.*

BS 3978, *Water for laboratory use.*

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