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SPECIFICATION FOR
KAOLIN FOR THE RUBBER INDUSTRY

SRI LANKA STANDARDS INSTITUTION

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SLS 650:1984

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SRI LANKA STANDARD

SPECIFICATION FOR KAOLIN FOR THE RUBBER INDUSTRY

FOREWORD

This Sri Lanka Standard specification was authorized for adoption and publication by the Council of the Sri Lanka Standards Institution on 1984-08-17, after the draft, finalized by the Drafting Committee on Kaolin had been approved by the Technical Advisory Committee on Rubber and Rubber Products and the Chemical Divisional Committee.

Kaolin is essentially a hydrated aluminium silicate derived from natural deposits and it is widely used as a semi reinforcing filler in the rubber industry to improve the hardness and tensile properties of the rubber compound.

All standard values in this specification are given in SI units.

For the purpose of deciding whether a particular requirement of this specification is complied with, the final value, observed or calculated, expressing the result of a test or analysis, shall be rounded off in accordance with CS 102. The number of significant places retained in the rounded off value should be the same as that of the specified value in this specification.

In the preparation of this specification, the assistance obtained from the publications of the International Organization for Standardization, and the Indian Standards Institution is gratefully acknowledged.

1 SCOPE

This specification prescribes requirements, methods of sampling and test for kaolin for use in the rubber industry.

2 REFERENCES

ISO 3262 Extenders for paints

CS 102 Presentation of numerical values

SLS 264 Kaolin for cosmetic industry

SLS 351 Rectified spirit

SLS 428 Random sampling methods.

3 REQUIREMENTS

3.1 Description

3.1.1 The material shall be natural mineral powder consisting essentially of hydrated aluminium silicate. It shall be free from extraneous impurities and grit.

3.1.2 The colour of the material shall be white or cream.

3.1.3 The material shall not contain any blueing or whitening substances.

3.2 Chemical and physical requirements

The material shall also comply with the requirements given in Table 1 when tested in accordance with the relevant methods prescribed in Column 4 of Table 1.

3.3 Physical form

The physical form of kaolin shall be such that when incorporated into the test recipe, (see Note) the unvulcanized mix shall have the kaolin properly dispersed, showing no evidence of uneven dispersion.

NOTE - The test recipe, the compounding procedure and the equipment used, shall be as agreed to between the purchaser and supplier.

4 PACKAGING AND MARKING

4.1 Packaging

The material shall be packed in paper bags or hessian bags with a suitable liner.

TABLE 1 - Physical and chemical requirements

Sl. No. (1)	Characteristic (2)	Limit (3)	Method of test Ref. to (4)
i	Silica : Alumina ratio, max.	1.5	Appendix A
ii	Particles less than 2 µm, % by mass, min.	75	ISO 3262:1975 Clause 9
iii	Particles less than 10 µm, % by mass, min.	95	ISO 3262:1975 Clause 9
iv	Residue on 45 µm, sieve, % by mass, max.	0.2	ISO 3262:1975 Clause 8
v	Residue on 125 µm, sieve, % by mass, max.	0.01	ISO 3262:1975 Clause 8
vi	Total copper (as Cu), mg/kg, max.	25	Appendix C
vii	Total manganese (as Mn), mg/kg, max.	50	Appendix D
viii	Total iron (as Fe_2O_3), % max.	1.5	Appendix B
ix	Matter volatile at 105 °C, % by mass max.	2.0	ISO 3262:1975 Clause 10
x	Loss on ignition at 1 000 °C, % by mass, max.	14	ISO 3262:1975 Clause 11
xi	pH of aqueous suspension (at 27 ± 2 °C)	4.5 to 9.5	ISO 3262:1975 Clause 13
xii	Relative density	2.5 to 2.6	Appendix E
xiii	Matter soluble in water, % by mass, max.	0.5	Appendix F
xiv	Matter soluble in hydrochloric acid, % by mass, max.	2.5	SLS 264:1974 Appendix A.8

4.2 Marking

Each bag shall be marked legibly and indelibly with the following information:

a) Name of material;

b) Name and address of manufacturer and/or supplier;

c) Gross mass and net mass in kg;

d) Date of packaging; and

e) Batch number.

4.3 The bags may also be marked with the Certification Mark of the Sri Lanka Standards Institution illustrated below on permission being granted for such marking by the Sri Lanka Standards Institution.

NOTE - The use of the Sri Lanka Standards Institution Certification Mark (SLS mark) is governed by the provisions of the Sri Lanka Standards Institution Act and the regulations framed thereunder. The SLS mark on products covered by a Sri Lanka Standard is an assurance that they have been produced to comply with the requirements of that standard under a well defined system of inspection, testing and quality control, which is devised and supervised by the Institution and operated by the producer. SLS marked products are also continuously checked by the Institution for conformity to that standard as a further safeguard. Details of conditions under which a permit for the use of the Certification Mark may be granted to manufacturers or processors may be obtained from the Sri Lanka Standards Institution.

5 SAMPLING

5.1 Lot

In a single consignment all the material coming from the same manufacturer/supplier shall constitute a lot.

5.2 General requirements of sampling

In drawing, preparing, storing and handling test samples, the following precautions and directions shall be observed.

5.2.1 Exposure to outer atmosphere during sampling shall be minimized.

5.2.2 Sampling instrument shall be clean and dry when used.

5.2.3 Precautions shall be taken to protect the samples, the material being sampled, the sampling instrument and the containers for samples from adventitious contamination.

5.2.4 The sample shall be placed in clean, dry, air-tight glass or other suitable container.

5.2.5 Each sample container shall be sealed air-tight, after filling and marked with necessary details of sampling.

5.2.6 The samples shall be stored in such a manner that during storage the properties of the material do not get affected.

5.3 Scale of sampling

5.3.1 Samples shall be tested from each lot for ascertaining the conformity of the material to the requirements of this specification.

5.3.2 The number of bags to be drawn from each lot shall be in accordance with Column 2 of Table 2.

TABLE 2 - Scale of sampling

Number of bags in the lot (1)	Number of bags to be selected from each lot (2)
Up to 10	All
11 to 200	5
201 to 500	10
501 to 2 000	15
2 001 and above	20

5.3.3 These bags shall be selected at random. In order to ensure randomness of selection random number tables as given in SLS 428 shall be used.

5.4 Preparation of samples

5.4.1 A small but approximately equal quantity of material shall be drawn from each of the bags selected as in 5.3.2 using an appropriate sampling instrument. All the portion of material taken from the sample bags shall be mixed together to form a composite sample.

5.4.2 The composite sample shall be suitably reduced by the method of coning and quartering or other suitable method to about 250 g.

5.5 Reference sample

If a reference sample is required the minimum size of the composite sample is about 750 g. Which shall be divided into three equal portions, to form three composite samples. One for the purchaser, another for the supplier, and third as the reference.

5.6 Number of tests

The composite sample shall be tested individually for all the requirements of this specification.

6 METHODS OF TEST

Tests shall be carried out as specified in the relevant Clauses of **ISO 3262:1975, SLS 264:1974** and Appendix A to Appendix **F.**

7 CONFORMITY TO STANDARD

The lot shall be declared as conforming to the requirements of this specification if the composite samples tested as in **5.6** satisfies the relevant requirements.

APPENDIX A

DETERMINATION OF SILICA : ALUMINA RATIO

A.1 PRINCIPLE

The silica alumina ratio is an indication of the chemical composition of the blend of complex hydrated aluminium silicates comprising the clay.

Silicon (calculated as SiO_2) is determined by the method given in A.2 and the aluminium (calculated as Al_2O_3) by that given in A.3.

A.2 DETERMINATION OF SILICON (as SiO_2)

A.2.1 Principle

The sample is fused with sodium carbonate. Silicon still insoluble in acid (*insoluble silica*) is determined by the loss in mass when it is converted to *volatile silicon* tetrafluoride by hydrofluoric acid. *Solubilised silicon* (That is the silicon rendered acid-soluble by fusion) is determined colorimetrically as silicomolybdate. Total silicon is reported as SiO_2 but this does not imply the presence of any free silica (SiO_2) in the sample.

A.2.2 Reagents

A.2.2.1 *Sodium carbonate* (anhydrous)

A.2.2.2 *Ammonium molybdate*, 80 g/l (0.065 M)

Dissolve 8.0 g of ammonium molybdate crystals $(NH_4)_6\ Mo_7O_{24}.4H_2O$) in 80 ml water then dilute to 100 ml in a 100 ml measuring cylinder.

A.2.2.3 *Ammonium ferrous sulphate*, 100 g/l, dissolve 10 g of ammonium ferrous sulfate crystals $(NH_4)_2SO_4.FeSO_4.6H_2O$) in 60 ml water plus 0.2 ml sulfuric acid 20% (V/V). Dilute to 100 ml in a 100-ml measuring cylinder.

NOTE - Use warm water for preparing this reagent.

A.2.2.4 *Ferric oxide solution*, 0.1 g/l, dissolve 0.0603 g of ammonium ferric sulphate crystals $(NH_4Fe(SO_4)_2.12H_2O)$ in 60 ml of water containing 1 ml sulfuric acid 20% (V/V), then dilute to 100 ml in a 100-ml measuring cylinder.

A.2.2.5 *Hydrochloric acid*, concentrated, 36% (m/m), (rel.den.=1.18 g/cm^3)

A.2.2.6 *Hydrofluoric acid*, 40% 20 g/l

A.2.2.7 *Silver nitrate*, 20 g/l, dissolve 2.0 g of silver nitrate ($AgNO_3$) crystals in water and dilute to 100 ml with water in a 100-ml measuring cylinder. Store in an amber glass bottle.

A.2.2.8 *Sulfuric acid*, 50% (V/V), cautiously add 500 ml sulfuric acid (rel. den. 1.84 g/cm^3) to 500 ml water, cool, then dilute to 1 litre in a 1-litre measuring cylinder.

A.2.2.9 *Sulfuric acid*, 20% (V/V), cautiously add 200 ml sulfuric acid (rel. den. 1.84 g/cm^3) to 800 ml water, cool, then dilute to 1 litre in a 1-litre measuring cylinder.

A.2.2.10 *Primary silica solution*, 1 000 µg/ml, (prepared from a quantity of high purity or precipitated silica which has been ignited at 1 100 °C to constant mass).

Fuse at 900 °C, about 1.0 g (weighed to the nearest milligram) of the ignited silica with 5 g of the sodium carbonate in a covered platinum crucible (20-ml). Extract the fused cake in hot water after placing the crucible in a 400-ml nickel beaker. Transfer the extract together with rinsings from the beaker and crucible to a 1-litre volumetric flask, cool and dilute to volume.

A.2.2.11 *Standard silica solution*, 50 µg/ml, dilute 50.0 ml of the primary silica solution with water to 1 000 ml in a volumetric flask.

A.2.2.12 *Standard silica solution*, 10 µg/ml, dilute 50.0 ml of the standard silica solution 50 µg/ml with water, to 250 ml, in a volumetric flask.

A.2.3 Apparatus

A.2.3.1 *Spectrophotometer,*

A.2.3.2 *Analytical balance,* capable of weighing to 0.001 g.

A.2.3.3 *Platinum dish,* of capacity approximately 20 ml.

A.2.4 Preparation of the calibration graph

To a series of 100-ml volumetric flasks add 0, 5.0, 10.0, 20.0, 30.0, and 35.0 ml of standard silica solution (10 µg/ml). The flasks will then contain 0, 50, 100, 200, 300 and 350 µg of silica.

Treat each aliquot as described under procedure for 'residual silica determination' (A.2.5.2). It is not necessary to prepare a "B" solution for each concentration of silica, one being sufficient for the calibration series.

Plot optical density values against silica concentrations in µg/ml to obtain a calibration curve.

A.2.5 Determination

A.2.5.1 *Insoluble silica determination*

Weigh about 1 g of the sample to the nearest milligram in a 20-ml platinum crucible.

Add 3 g of sodium carbonate in portions to the crucible, mixing thoroughly between additions with a platinum stirring rod, reserving about 0.3 g to cover the mixture. Place the lid on the crucible then cautiously heat over a Meker or similar type burner until the crucible contents are molten. Maintain at a full red heat for 30 minutes then allow to cool.

Place the crucible and lid in a 600-ml beaker, add 50 ml of hot water, cover with a watch glass then carefully add 30 ml of the hydrochloric acid. Place the beaker on a low temperature hotplate (85 ± 5 °C) and heat until the molten material becomes detached from the crucible. Remove the crucible from the beaker, rinse with a jet of hot water, and remove adherent particles by rubbing with a rubber tipped glass rod. Remove the crucible lid and clean in a similar fashion.

Evaporate the contents of the beaker to dryness on the low temperature hotplate, then place in an oven at 105 ± 5 °C for 1 hour.

Allow the beaker to cool then drench the residue with 10 ml of the hydrochloric acid and dilute with 90 ml of hot water. Warm to dissolve soluble salts and then filter through a 12.5 mm diameter medium grade ashless filter paper (Whatman No. 40 or equivalent), collecting the filtrate in a 500-ml graduated flask. Wash the filter and beaker thoroughly with hot water, removing adherent particles with a rubber tipped glass rod. Continue washing until chlorides have been removed from the filter (test a portion of the washings emerging from the funnel with a drop of the silver nitrate solution). Reserve the filtrate and washings (1).

Transfer the filter paper to a platinum crucible (20 ml), wipe the inside of the beaker with a portion of dampened filter paper, and place in the crucible. Dry the crucible and contents in an oven and then carefully ignite over a Meker type burner. Once the carbonaceous matter has been removed, ignite at a temperature over 1 100 °C.

Cool the crucible in a desiccator and weigh to the nearest 0.1 mg (m_1). Moisten the silica residue with water, add 10 drops of sulfuric acid 20% (V/V) then 10 ml of the hydrofluoric acid. Place the crucible and contents on a heated sand tray and evaporate under a fume hood until the evalution of white sulfuric acid fumes ceases. Expel residual sulfuric acid by cautious heating over the burner, and then heat to about 1 000 °C for 5 minutes. Cool in a desiccator and weigh (m_2).

Mass of insoluble silica (g) = $m_1 - m_2$.

Fuse the residue in the crucible with 0.5 g of the sodium carbonate, cool and extract with hot water. Acidify the extract by dropwise addition of hydrochloric acid and then combine it with the reserved filtrate (1) and dilute to 500 ml to form a combined diluted filtrate (2).

A.2.5.2 *Residual silica determination*

Transfer two 10 ml aliquots (A and B) of the combined diluted filtrate (2) to two 100-ml volumetric flasks.

NOTE - The blue silico-molybdate colour will be generated in A, *while* B *will contain a compensating solution.*

To each add 6 ml *of the ferric oxide solution and 1.0* ml *of the hydrochloric acid. Bring the volume in each flask to 50 ± 1* ml, *by adding distilled water.*

To flask A add 10 ml *of the ammonium molybdate solution, mix and allow to stand 5 minutes then add 12* ml *sulfuric acid, 50% V/V mix well and allow to stand another 5 minutes.*

To flask B add 12 ml *of sulfuric acid 50% V/V then 10* ml *of the ammonium molybdate solution, mix and allow to stand 5 minutes.*

To each flask add 10 ml of ammonium ferrous sulfate 10% m/V, dilute to 100 ml immediately, mix and allow to stand for 15 minutes.

Measure the optical density of solution A with reference to solution B in 10.0 mm path cells in a spectrophotometer at a wavelength of 800 nm. Refer the value for optical density to a calibration curve to derive the mass of residual silica present in the aliquot taken for measurement.

$$\text{Mass of residual silica (g)} = \frac{\text{mass in aliquot (µg/ml)} \times 50}{10^6}$$

A.2.6 Calculation

$$\% \text{ Silicon (reported as } SiO_2) = \left[\frac{\text{Mass of insoluble silica (g)} + \text{Mass of residual silica (g)}}{\text{Mass of sample (g)}}\right] \times 100$$

A.3 DETERMINATION OF ALUMINIUM (as Al_2O_3)

A.3.1 Principle

Aluminium is rendered acid-soluble by fusion with sodium carbonate. Any iron is removed by cupferron and then EDTA is added to complex the aluminium. Excess EDTA is back-titrated with a standard zinc solution.

A.3.2 Reagents

A.3.2.1 *Chloroform*

A.3.2.2 *Ethanol (ethyl alcohol)*, anhydrous.

A.3.2.3 *Ammonia solution*, concentrated 35% (m/m), rel. den.= 0.880 g/cm^3

A.3.2.4 *Ammonium acetate buffer solution*

To 500 ml water, add 120 ml glacial acetic acid, stir then add 74 ml ammonia solution (A.3.2.3) with stirring, Cool and dilute to one litre in a measuring cylinder.

A.3.2.5 *Cupferron solution*, 6% m/v, reagent solution, dissolve 6.0 g of cupferron [$C_6H_5.N(NO)ONH_4$] in 50 ml of water and then dilute to 100 ml in a measuring cylinder. Filter to remove any insoluble matter. Prepare this reagent freshly.

A.3.2.6 *Hydrochloric acid,* concentrated (rel. den. = 1.18 g/cm^3)

A.3.2.7 *Zinc 0.05 M, standard reference solution,* dissolve 3.2685 g of pure zinc chips in 15 ml of the hydrochloric acid (A.3.2.6) and dilute to 1 litre in a volumetric flask.

A.3.2.8 *EDTA, 0.05 M , standard volumetric solution,* dissolve 18.612 g of the di-sodium salt of ethylene diamine tetra-acetic acid $[CH_2.N(CH_2.COOH)(CH_2.COONa)]_2.2H_2O$ in 800 ml water, and dilute to 1 litre in a volumetric flask. Standardize against the zinc standard reference solution (A.3.2.7) and in A.3.3 below.

A.3.2.9 *Bromophenol blue, 0.1% m/v, indicator solution,* dissolve 0.10 g of bromophenol blue in 1.5 ml sodium hydroxide solution (0.1 M) then dilute to 100 ml in a measuring cylinder.

A.3.2.10 *Dithizone, 0.025%, m/v, indicator solution,* dissolve 0.025 g of dithizone ($C_6H_5.N.N.CS.NH.NH.C_6H_5$) in 80 ml anhydrous ethanol (A.3.2.2).

A.3.3 Standardization of EDTA solution 0.05 M

Pipette 20.0 ml of the EDTA solution (0.05 M approx., A.3.2.8) into a 500-ml conical flask, add 4 drops of bromophenol blue (A.3.2.9) followed by ammonium acetate buffer (A.3.2.4) until the indicator colour changes to blue from yellow. Add 10 ml of ammonium acetate buffer excess. Dilute with water to approximately 100 ml and then add an equal volume of ethanol (A.3.2.2). Add 1 ml to 2 ml of dithizone solution (A.3.2.10) and titrate with standard zinc solution 0.05 M (A.3.2.7) to a permanent pink end-point. Record the volume of titrant.

Divide the volume of EDTA solution used (20.0 ml) by the volume of titrant to provide a factor which must be applied to the volume of EDTA used in the aluminium determination in order that it may be expressed as exactly 0.05 M for the calculation.

A.3.4 Procedure

Transfer a 100 ml aliquot of the reserved silica filtrate (2) from (A.2.5.1) to a 250-ml separating funnel, add 20 ml of the hydrochloric acid, mix the contents and cool. Add 2 ml of the cupferron solution (A.3.2.5) and mix. Then extract the cupferrates by shaking with 20 ml of the chloroform (A.3.2.1) for 30 seconds. Allow the chloroform extract to separate and then run off and discard. Extract the solution with a further 20 ml of chloroform, allow the layers to separate and then test the aqueous layer with 1 ml of cupferron solution. If all cupferrates have been extracted a transient white precipitate of the reagent will form. Continue extraction with fresh portions of chloroform until cupferrates and excess cupferron have been removed, as indicated by a water white chloroform layer (excess cupferron imparts a green colour to chloroform). Discard all chloroform extracts.

Quantitatively transfer the aqueous layer into a 500-ml conical flask and heat to boiling to remove chloroform traces. Cool, add 4 drops of bromophenol blue (A.3.2.9) followed by careful addition of ammonia solution (A.3.2.3) to change the indicator colour from yellow to blue. Immediately acidify by dropwise addition of hydrochloric acid (A.3.2.6) adding 4 to 6 drops excess. From a burette, dispense sufficient EDTA solution (A.3.2.8) to complex all aluminium present and provide at least 2 ml excess. Add ammonium acetate buffer (A.3.2.4) until the bromophenol blue indicator colour changes from yellow to blue, then add 10 ml excess. Heat the solution to boiling and boil for 10 minutes then cool to room temperature.

Dilute the solution with an equal volume of ethanol (A.3.2.2) add 1 ml to 2 ml of dithizone solution (A.3.2.10) and then titrate with zinc chloride solution (A.3.2.7) to a permanent pink end-point.

A.3.5 Calculation

% Aluminium (expressed as Al_2O_3)

$$= \frac{(\text{Vol. EDTA 0.05 M} - \text{Vol. Zinc 0.05 M})\ \text{ml} \times 0.00255 \times 5 \times 100}{\text{Sample mass (g)}}$$

A.4 CALCULATION OF SILICA : ALUMINA RATIO

$$\text{Silica : Alumina Ratio} = \frac{\%\ \text{silicon (calculated as } SiO_2)}{\%\ \text{aluminium (calculated as } Al_2O_3)}$$

A.5 EXPRESSION OF RESULTS

Express the result to the nearest 0.01.

APPENDIX B

DETERMINATION OF IRON

B.1 PRINCIPLE

Any iron in the sample is rendered acid-soluble by fusion with sodium carbonate then total iron is determined colorimetrically with 2,2' bipyridyl.

B.2 REAGENTS

B.2.1 *Ammonium acetate solution*, 20% m/v, dissolve 200 g ammonium acetate ($CH_3COO\ NH_4$) in 600 ml of water, then dilute to one litre in a measuring cylinder.

B.2.2 *2,2' bipyridyl solution*, 0.2% m/v, dissolve 0.2 g of 2.2' bipyridyl ($C_5H_4N_2$) in 60 ml of water with gentle warming. Cool and dilute to 100 ml in a measuring cylinder. Use within four weeks of preparation.

B.2.3 *Hydroxylammonium chloride*, 50% m/v, dissolve 50 g of hydroxylammonium chloride ($HO.NH_3Cl$) in 50 ml of water, then dilute to 100 ml in a measuring cylinder.

B.3 CALIBRATION

B.3.1 Reagents

B.3.1.1 *Primary iron solution*, dissolve 1.000 ± 0.001 g of high purity iron metal chips in a mixture of 10 ml of water and 5 ml of nitric acid (rel. den. 1.42 g/cm^3). Boil to expel oxides of nitrogen. Cool and dilute to one litre in a volumetric flask.

1 ml of this solution contains 1.000 ± 1 µg Fe.

B.3.1.2 *Standard iron solution*, 50 µg/ml, pipette 50.0 ml of primary iron solution (B.3.1.1) into a one-litre volumetric flask, add 10 ml of hydrochloric acid (rel. den. 1.18 g/cm^3) then dilute to one litre with water and mix.

B.3.1.3 *Standard iron solution*, 10 µg/ml, pipette 50.0 ml of standard iron solution 50 µg/ml (B.3.1.2) into a 250-ml volumetric flask, add 2.5 ml hydrochloric acid (rel. den. 1.18 g/cm^3) then dilute to 250 ml with water and mix.

B.3.2 Preparation of the calibration graph

To a series of 50-ml volumetric flasks add 0, 5.0, 10.0, 20.0, 25.0 and 30.0 ml of standard iron solution (10 µg/ml). The flasks will then contain 0, 50, 100, 200, 250 and 300 µg of iron (Fe).

Take each aliquot through the colour development procedure (B.4).

Measure optical densities as in B.4.

Plot optical density values against number of µg of iron in each flask to obtain a calibration curve.

B.4 PROCEDURE

Pipette a 20.0 ml aliquot of the combined diluted filtrate (2) (A.2.4) into a 50-ml volumetric flask.

Add 0.5 ml of the hydroxylammonium chloride solution (B.2.3), 2 ml of the 2,2' bipyridyl solution (B.2.2) 10 ml of ammonium acetate solution (B.2.1), dilute to 50 ml with water and mix.

Allow to stand for 10 minutes, measure the optical density of the solution with reference to water in 10.0 mm length cells, on a spectrophotometer at a wavelength of 520 nm.

Refer the optical density value to the calibration curve (B.3.2) to derive the mass of iron present in the aliquot.

If the optical density is greater than the range covered by the calibration curve (B.3.2), repeat the procedure (B.4) using a smaller aliquot of the combined reserved filtrate (2) (A.2.5) and apply an appropriate factor in the calculation.

B.5 CALCULATION

% iron (calculated as Fe_2O_3)

$$= \frac{\text{(mass of Fe in aliquot) } \mu g \times 1.43 \times 25 \times 10^{-6}}{\text{Sample mass (g)}}$$

B.6 EXPRESSION OF RESULTS

Express the result to the nearest 0.01.

APPENDIX C

DETERMINATION OF COPPER

Two methods have been specified for determination of copper. Method 1 shall be the reference method and shall be carried out in case of any dispute.

C.1 METHOD 1

C.1.1 Principle

Treatment with perchloric and hydrofluoric acids renders most clays soluble. Any matter still insoluble is fused with sodium carbonate, and the resulting extract is combined with the original acid extract to provide a complete solution prior to copper determination by atomic absorption spectrophotometry at 324.5 nm.

C.1.2 Reagents

C.1.2.1 *Sodium carbonate anhydrous*

C.1.2.2 *Hydrochloric acid*, concentrated, 36% m/m, rel, den, 1.18 g/cm^3

C.1.2.3 *Hydrofluoric acid*, 40% m/m, rel. den. 1.13 g/cm^3

C.1.2.4 *Perchloric acid*, 60% m/m

C.1.2.5 *Primary copper solution*, dissolve 1.000 ± 0.001 g of high purity copper metal chips in a mixture of 10 ml of water and 5 ml of nitric acid (rel. den. 1.42 g/cm^3). Boil to expel oxides of nitrogen. Cool and dilute to one litre in a volumetric flask.

1 ml of this solution contains 1.000 ± 1 µg Cu.

C.1.2.6 *Standard copper solution*, 50 µg/ml, pipette 50.0 ml of primary copper solution (C.1.2.5) into a one-litre volumetric flask, add 5 ml nitric acid (rel. den. 1.42 g/cm^3) then dilute to one litre with water and mix.

C.1.2.7 *Standard copper solution*, 10 µg/ml, pipette 50.0 ml of standard copper solution 50 µg/ml into a 250-ml volumetric flask, add 1 ml of nitric acid (rel. den. 1.42 g/cm^3) then dilute to 250 ml with water and mix.

C.1.3 Apparatus

C.1.3.1 *Atomic absorption spectrophotometre*, fitted with an air acetylene burner.

C.1.3.2 *Analytical balance*, capable of weighing to 0.001 g.

C.1.3.3 *Platinum dish*, of capacity approximately 20 ml.

C.1.4 Preparation of the calibration graph

C.1.4.1 *Preparation of standard matching solutions*, to a series of 50-ml volumetric flasks add by measuring pipette 0.5, 2.5, 5.0, 10.0, 15.0 and 25.0 ml of standard copper solution, 10 µg/ml (C.1.2.7). Dilute each to 50 ml to give matching solutions of 0.1, 0.5, 1.0, 2.0, 3.0 and 5.0 µg/ml.

C.1.4.2 *Spectrometric measurements*, aspirate each of the standard matching solutions in turn, into the flame of the atomic absorption spectrometer and record their absorbances at a wavelength of 324.5 nm, following the instructions of the instrument manufacturer.

C.1.4.3 *Plotting the graph*, plot the graph having, for example, the copper contents, in-micrograms per cubic centimetre, as abscissa and the corresponding values of absorbance as ordinates.

C.1.5 Determination

C.1.5.1 *Preparation of the test solution*, weigh about 2 g of sample to the nearest 0.001 g into a platinum dish (C.1.3.3) disperse with water, add 5 ml of perchloric acid (C.1.2.4) and 10 ml of hydrofluoric acid (C.1.2.3). Place the dish on a heated sand tray and evaporate to perchloric acid fumes. Remove from the sand tray and cool. Add 10 ml of hydrofluoric acid (C.1.2.3), replace on the sand tray and evaporate the contents of the dish to dryness.

Treat the residue with 5 ml perchloric acid (C.1.2.4), rinse inside the walls of the dish with a small quantity of water, then evaporate to dryness.

Treat the residue with 5 ml of hydrochloric acid (C.1.2.2) and 20 ml of water, then allow the mixture to digest on the heated sand tray until salts are in solution.

Filter through a Whatman No. 40 or equivalent medium grade ashless filter paper, collecting the filtrate in a 100-ml volumetric flask. Wash the dish and filter with hot water into the 100-ml volumetric flask containing the filtrate. Place the filter in a platinum crucible (20-ml), dry, then ignite. Fuse the residue with 0.5 g sodium carbonate (anhydrous), cool and treat with hot water. Acidify the solution by adding hydrochloric acid (C.1.2.2) dropwise then combine with the filtrate. Dilute to 100 ml and mix. Transfer this test solution to a dry polyethylene bottle.

C.1.5.2 *Blank test*, carry out a blank test simultaneously with the determination, using the same reagents and same procedures, but ommitting the test portion.

C.1.5.3 *Spectrometric measurements*

Aspirate the test solution (C.1.5.1) and the blank test solution (C.1.5.2) into the flame of the atomic absorption spectrometer and measure their absorbances at 324.5 nm, following the instructions of the instrument manufacturer. Repeat this procedure and record the mean values of absorbance of the test solution and the blank test solution.

Aspirate water into the flame after each measurement.

C.1.6 Calculation

By reference to the calibration graph (C.1.4.3) determine the copper contents. Corresponding to the absorbances of the test solution and the blank test solution.

The total copper content of the sample, expressed in milligrams per kilogram, is given by the formula.

$$\frac{100\ (M_1 - M_2)}{m}$$

where,

M_1 is the copper content, in micrograms per cubic centimetre of the test solution;

M_2 is the copper content, in micrograms per cubic centimetre of the blank test solution; and

m is the mass, in grams, of the test solution.

C.1.7 Expression of results

Express the result to the nearest 0.1 mg/kg.

C.2 METHOD 2

C.2.1 Principle

Copper is determined colorimetrically using sodium diethyldithiocarbamate by visual comparison.

C.2.2 Apparatus

C.2.2.1 *Nessler cylinders*, 100 ml capacity.

C.2.3 Reagents

C.2.3.1 *Ammonium hydroxide*, concentrated, 18 M (relative density 0.90).

C.2.3.2 *Ammonium citrate solution*, dissolve 100 g of citric acid in 100 ml of ammonium hydroxide and upto 200 ml with water.

C.2.3.3 *Gum arabic solution*, 5 per cent (m/V).

C.2.3.4 *Sodium diethyldithiocarbamate solution*, dissolve 1.0 g of sodium diethyldithiocarbamate in one litre of copper-free water. Keep in an amber coloured bottle and protect from strong light.

C.2.3.5 *Standard copper solution*, dissolve 0.3139 g of copper sulfate crystals ($CuSO_4.5H_2O$) in copper-free water and make up the volume of 100 ml with copper-free water. Take 100 ml of this solution and further dilute to 1 000 ml with copper-free water. One millilitre of this solution is equivalent to 0.01 mg of copper oxide (as CuO).

C.2.3.6 *Sulfuric acid*, 98% (m/m) solution. (rel. den. 1.84 g/cm^3).

C.2.3.7 *Nitric acid*, rel. den. 1.42 g/cm^3.

C.2.4 Procedure

C.2.4.1 *Preparation of the test solution*

Weigh to the nearest milligram, 2.0 g of the dry sample and mix with 8 g of anhydrous sodium carbonate (C.1.2.1), and fuse in a platinum crucible until the melt is clear. Leach out the melted mass with water into a porcelain dish, and then put the crucible in the same dish. Add about 20 ml of water and heat on a water-bath until the product is disintegrated. Remove the crucible after washing in the dish. Evaporate the contents of the dish to dryness. Add a mixture of 12 ml of concentrated sulfuric acid and 2 ml of concentrated nitric acid. Evaporate till fumes of sulfur trioxide appear, dilute to exactly 500 ml and filter through a filter paper to remove silica. Use this prepared test solution for the test under D.2.

NOTE - In case the prepared sample solution is turbid, add a few drops of ferric chloride solution (approximately 5 per cent (m/v), boil and precipitate twice with ammonium hydroxide solution, and filter.

C.2.4.2 *Colorimetric measurement*

Pipette 25 ml of the prepared test solution into a small conical flask or beaker. Drop into it a small piece of litmus paper and make the solution just alkaline with ammonium hydroxide. Add 2.5 ml of

ammonium hydroxide in excess and heat to boiling. Allow to stand on a water-bath for one hour to ensure complete precipitation of aluminium hydroxide and then filter through filter paper (Whatman No. 1 or equivalent), into a Nessler cylinder, washing the filter paper with two or three small portions of hot water. To the solution in the Nessler cylinder, add 5 ml of ammonium citrate, 5 ml of gum arabic solution, 10 ml of ammonium hydroxide solution and 10 ml of sodium diethyldithiocarbamate solution in the order mentioned. Dilute to 100 ml mark and mix well. To the other Nessler cylinder containing an equal aliquot of blank solution carried through the entire analysis in the same manner as the prepared test solution, add equal amounts of the same reagents, dilute to about 90 ml and mix. Add to this solution standard copper solution from a 10-ml burette until its colour matches that of the material under test after diluting to the same volume. Mix well after each addition of standard copper solution.

C.2.4.2.1 If the colour produced with the prepared test solution is too deep for comparison, a smaller aliquot of the prepared test solution from the acid digestion should be used.

C.2.5 Calculation

$$\text{Copper content as Cu in mg/kg} = \frac{2V \times 79}{m}$$

where,

V = volume, in ml, of standard copper solution used for the blank, and

m = mass, in g, of the dry material taken for the test.

C.2.6 Expression of results

Express the result to the nearest 0.1 mg/kg.

APPENDIX D

DETERMINATION OF MANGANESE

Two methods have been specified for determination of manganese. Method 1 shall be the references method and shall be carried out in case of any dispute.

D.1 METHOD 1

D.1.1 Principle

After rendering the manganese acid-soluble and removing silicon as in Appendix C total manganese is determined by atomic absorption spectrophotometry at 279 nm.

D.1.2 Reagents

D.1.2.1 *Sodium carbonate,* (see C.1.2.1).

D.1.2.2 *Hydrochloric acid,* (see C.1.2.2).

D.1.2.3 *Hydrofluoric acid,* (see C.1.2.3).

D.1.2.4 *Perchloric acid,* (see C.1.2.4).

D.1.2.5 *Primary manganese solution,* dissolve 1.000 ± 0.001 g of high purity oxide-free manganese metal in a mixture of 50 ml of water and 5 ml of nitric acid (rel. den. 1.42). Boil to expel oxides of nitrogen. Cool and dilute with water to one litre in a volumetric flask.

1 ml of this solution contains 1 000 ± 1 µg Mn.

D.1.2.6 *Standard manganese solution,* 50 µg/ml, pipette 50.0 ml of primary manganese solution (D.1.2.5) into a one litre volumetric flask, add 5 ml of nitric acid (rel, den. 1.42 g/cm^3), then dilute to one litre with water and mix.

D.1.2.7 *Standard manganese solution,* 10 µg/ml, pipette 50.0 ml of standard manganese solution 50 µg/ml (D.1.2.6) into a 250-ml volumetric flask, add 1 ml of nitric acid (rel. den. 1.42 g/cm^3); then dilute to 250 ml with water and mix.

D.1.3 Apparatus

As specifiied in C.1.3.

D.1.4 Preparation of the calibration graph

D.1.4.1 *Preparation of standard matching solution,* to a series of 50-ml volumetric flasks and 0.5, 2.5, 5.0, 10.0 and 25.0 ml of standard manganese solution, 10 µg/ml (D.1.2.7). Dilute each to 50 ml to give matching solutions of 0.1, 0.5, 1.0, 2.0, 5.0, and 5.0 µg/ml.

D.1.4.2 *Spectrometric measurements*, Aspirate each of the standard matching solutions, in turn, into the flame of the atomic absorption spectrometer and record their absorbance at a wavelength of 270 nm, following the instructions of the instrument manufacturer.

Aspirate water into the flame after each measurement.

D.1.4.3 *Plotting the graph*, plot the graph having, for example, the manganese contents, in micrograms per cubic centimetre, as abscissa and the corresponding values of absorbance, ordinates.

D.1.5 Determination

D.1.5.1 *Preparation of the test solution*, use the test solution prepared as described C.1.5.1.

D.1.5.2 *Blank test*, carry out a blank test simultaneously with the termination, using the same reagents and same procedures, but ommitting the test portion.

D.1.5.3 *Spectrometric measurements*, aspirate the test solution and the blank test solution into the flame of the atomic absorbtion spectrometer and measure their absorbance at 279 nm, following the instructions of the instrument manufacturer. Repeat this procedures and record the mean values of absorbance of the test solution and the blank test solution.

Aspirate water into the flame after each measurement.

D.1.6 Calculation

By reference to the calibration graph (D.1.4.3), determine the manganese contents, corresponding to the absorbances of the test solution and the blank test solution.

The total manganese content of the sample, expressed in milligrams per kilograms is given by the formula.

$$\frac{100\ (M_1 - M_2)}{m}$$

where,

M_1 is the manganese content, micrograms per cubic centimetre of the test solution;

M_2 is the manganese content, in micrograms per cubic centimetre of the blank test solution; and

m is the mass in grams, of the test portion.

D.1.7 Expression of results

Express the result to the nearest 0.1 mg/kg.

D.2 METHOD 2

D.2.1 Principle

Manganese is determined by comparing the colour produced by oxidation with periodate against the colour of a standard potassium permanganate solution.

D.2.2 Apparatus

D.2.2.1 *Nessler cylinders*, 50 ml capacity.

D.2.3 Reagents

D.2.3.1 *Phosphoric acid*, 85 per cent (m/m).

D.2.3.2 *Standard potassium permanganate solution*, Prepare a dilute solution of potassium permanganate by diluting to 50 ml in a volumetric flask a quantity of recently standardized solution in accordance with the following formula:

$$A = \frac{1.7620}{M}$$

where,

A = volume in ml of the standard potassium permanganate solution to be made up to a volume of 50 ml, and

M = molarity of the standard potassium permanganate solution.

One millilitre of this solution is equivalent to 0.1 mg of manganese oxide (as MnO). The solution shall be freshly prepared.

D.2.3.3 *Potassium periodate*, solid.

D.2.4 Procedure

Transfer 125 ml of the prepared test solution (see C.2.4.1) to a 250-ml beaker and evaporate to 75 ml. Add 10 ml of phosphoric acid, sprinkle 0.5 g of potassium periodate into the solution and bring it to boil. Cool slightly, sprinkle again 0.1 g of potassium periodate and boil. When the colour appears to have developed to the maximum, place the beaker on a steam bath and keep for 15 minutes. If there is any doubt about the completeness of the reaction, add more potassium periodate.

After 15 minutes remove the beaker and cool to room temperature. Place the solution in a Nessler cylinder and dilute to mark with water. Place and equal aliquot of a blank solution carried through the entire analysis in the same manner as the prepared test solution in the other Nessler cylinder and dilute almost to the mark. To this solution add standard potassium permanganate solution from a 10-ml burette until its colour matches that of the material under test when diluted to the same volume.

D.2.5 Calculation

$$\text{Manganese content as Mn in mg/kg} = \frac{4V \times 77}{m}$$

where,

V = volume, in ml, of standard potassium permanganate solution used for the blank; and

m = mass, in g, of the dry sample taken for the test (see C.2.4.1)

D.2.6 Expression of results

Express the result to the nearest 0.1 mg/kg.

APPENDIX E

DETERMINATION OF RELATIVE DENSITY

E.1 APPARATUS

E.1.1 *Specific gravity bottle*, 25 ml capacity having a ground in capillary stopper.

E.1.2 *Vacuum apparatus*, with a vacuum desiccator and a vacuum pump capable of reducing the pressure to not greater than 2 kPa.

E.2 PROCEDURE

E.2.1 Weigh about 20 g of the material and dry by heating at 105 ± 2 °C for 2 h and allow to cool to room temperature in a desiccator.

Wash and dry the specific gravity bottle, and stopper and weigh to the nearest milligram. Introduce in to the bottle by means of a dry funnel 10 g of the dried material so that the bottle is not more than half filled. Reweigh the stoppered bottle to the nearest milligram.

Fill the bottle with water to cover the test portion completely to a depth of about 15 mm. Allow the bottle to remain in the vacuum desiccator under reduced pressure (not greater than 2 kPa) for about 4 h or until no air bubbles are visible in the liquid. Tap the desiccator occasionally to assist in removing entrained air.

E.2.2 Remove the bottle from the desiccator, fill it completely with water. Insert the stopper carefully so that the excess liquid fills the capillary. Wipe of the water from the stopper. Allow to stand for 15 min at 27 ± 2 °C and weigh to the nearest milligram.

E.2.3 Empty the bottle fill it with water and weigh after bringing it to 27 ± 2 °C.

E.3 CALCULATION

$$\text{Relative density } 27^{\circ}/27^{\circ}\text{C} = \frac{(m_2 - m_1)}{(m_4 - m_1) - (m_3 - m_2)}$$

where,

m_1 = mass, in g, of the specific gravity bottle;

m_2 = mass, in g, of specific gravity bottle and sample;

m_3 = mass, in g, of specific gravity bottle with sample and water; and

m_4 = mass, in g, of specific gravity bottle and water.

APPENDIX F

MATTER SOLUBLE IN WATER

F.1 REAGENTS

F.1.1 *Rectified spirit*, (see SLS 351).

F.1.2 *Bromophenol blue indicator solution*, dissolve 0.1 g of bromophenol blue in 100 ml of rectified spirit.

F.1.3 *Hydrochloric acid*, dilute, approximately 0.1 M.

F.2 PROCEDURE

F.2.1 Weigh to the nearest milligram 10 g of the dried material (see E.2.1) in a 250-ml beaker. Add 5 ml of rectified spirit to wet the sample thoroughly. Add 200 ml of water, boil the suspension for 5 minutes and allow to cool to room temperature. Add sufficient bromophenol blue indicator to give a visible colour, and then add dilute hydrochloric acid until the blue colour disappears.

NOTE - Bromophenol blue turns yellow at about pH 4 at which point flocculation occurs and clear filtration is obtained.

F.2.2 Transfer the contents of the beaker to a 250-ml volumetric flask, dilute to the mark with neutral distilled water and mix well by shaking. Filter through a filter paper; rejecting the first 50 ml of filtrate. Place 100 ml of the clear filtrate into a tared porcelain dish and evaporate to dryness on a water bath. Dry the residue at 105 ± 2 °C, cool and weigh until constant mass is obtained.

F.3 CALCULATION

$$\text{Matter soluble in water, per cent by mass} = 250 \times \frac{m_1}{m}$$

where,

m_1 = mass, in g, of the residue obtained; and

m = mass, in g, of the material taken for the test.

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