

SRI LANKA STANDARD 645 : PART 6 : 1990

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METHODS OF TEST FOR

FERTILIZERS

PART 6 - DETERMINATION OF CALCIUM AND

MAGNESIUM CONTENT

SRI LANKA STANDARDS INSTITUTION

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PART 6 : DETERMINATION OF CALCIUM AND MAGNESIUM CONTENT

SLS 645:Part 6:1990

Gr. 8

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SRI LANKA STANDARDS INSTITUTION,
53, Dharmapala Mawatha,
Colombo 3,
Sri Lanka.

SRI LANKA STANDARD
METHODS OF TEST FOR FERTILIZERS
PART 6 : DETERMINATION OF CALCIUM AND MAGNESIUM CONTENT

FOREWORD

This Sri Lanka Standard was authorized for adoption and publication by the Council of the Sri Lanka Standards Institution on 1990-09-24, after the draft, finalized by the Drafting committee on Fertilizers had been approved by the Chemicals Divisional Committee.

This part is one of the series of standards on testing of fertilizers. Other parts which have already been issued cover the determination of nitrogen, moisture, biuret, potassium and phosphorus.

This part of the standard consists of three sections as follows :

- Section 1 : Determination of calcium and magnesium content - EDTA titrimetric method.
- Section 2 : Determination of calcium content - Atomic absorption spectrophotometric method.
- Section 3 : Determination of magnesium content - Atomic absorption spectrophotometric method.

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

In reporting the result of a test or an analysis made in accordance with this standard, if the final value, obtained or calculated is to be rounded off, it shall be done in accordance with CS 102.

In the preparation of this standard, the assistance derived from the American Society for Testing and Materials and Fertilizers and Feeding Stuffs regulations of the United Kingdom (1978) is gratefully acknowledged.

1 SCOPE

This part of the standard prescribes methods for the determination of calcium and magnesium in fertilizers including fertilizer mixtures.

2 REFERENCES

- CS 102 Presentation of numerical values.
- CS 124 Test sieves.
- SLS 559 Sampling of fertilizers.

3 PREPARATION OF THE TEST SAMPLE

Reduce the test sample specified as in Clause 6 of SLS 559 : 1982 to a quantity sufficient for analysis. Grind not less than 225 g of the reduced sample without prior sieving. For fertilizer materials and moist fertilizer mixtures, grind to pass through a sieve of 1-mm aperture size. For dry mixtures that tend to segregate, grind to pass through a sieve of 350- μ m aperture size. Grind as rapidly as possible to avoid loss or gain of moisture during the operation. Mix thoroughly and store in tightly stoppered bottles.

**SECTION 1 : DETERMINATION OF CALCIUM AND MAGNESIUM CONTENT - EDTA
TITRIMETRIC METHOD**

1 PRINCIPLE

The sample is ashed and dissolved in hydrochloric acid or, if it contains no organic substances, it is dissolved directly in dilute hydrochloric acid. The calcium content of the extract is determined by titration with EDTA in the presence of HHSNNA indicator. The calcium and magnesium content of the extract is determined by titration with EDTA in the presence of eriochrome black-T indicator.

2 REAGENTS

Unless specified otherwise, reagents of analytical grade and distilled water or water of equivalent purity shall be used.

2.1 *Hydrochloric acid*, concentrated (rel.den. = 1.18)

2.2 *Hydrochloric acid*, 50 per cent (V/V) solution prepared by using concentrated hydrochloric acid (rel.den. = 1.18)

2.3 *Calcium standard solution*

Dissolve 2.4973 g of calcium carbonate, previously dried at 105 °C for one hour, in 120 ml of 10 per cent (V/V) hydrochloric acid solution prepared by using concentrated hydrochloric acid (rel.den. = 1.18). Boil the solution in order to drive off the carbon dioxide, cool and dilute to 1 litre with water.

One millilitre of this solution contains 1 mg of calcium.

2.4 *Ammonia solution*, 10 per cent (V/V) solution prepared by using concentrated ammonia solution (rel.den. = 0.90)

2.5 *Potassium hydroxide - potassium cyanide solution*

Dissolve 280 g of potassium hydroxide and 66 g of potassium cyanide in 1 litre of water.

2.6 HHSNNA indicator

Triturate 0.5 g of the solid 2-hydroxy-(2-hydroxy-4-sulfo-1-naphthazo)-3-naphthoic acid (HHSNNA) with 50 g of anhydrous sodium sulphate in a glass mortar until the HHSNNA is evenly distributed. Store in a amber glass bottle.

2.7 Disodium dihydrogen ethylenediamine tetraacetate (EDTA), 0.01 mol/l solution

Dissolve 3.722 g of disodium dihydrogenethylenediamine tetraacetate dihydrate in water and dilute to 1 litre.

2.8 Magnesium standard solution

Dissolve 10.1558 g of crystalline magnesium sulfate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) in water and dilute to 1 litre.

One millilitre of this solution contains 1 mg of magnesium.

2.9 Buffer solution, p^H_{10}

Dissolve 67.5 g of ammonium chloride in 200 ml of water. Add 570 ml of concentrated ammonia solution (rel.den. = 0.90) and dilute to 1 litre.

2.10 Potassium cyanide solution

Dissolve 2 g of potassium cyanide in 100 ml of water.

2.11 Eriochrome black - T - indicator

Prepare the indicator as given in (2.11.1) or (2.11.2)

2.11.1 Dissolve 0.2 g of eriochrome black - T in 50 ml of methanol containing 2 g of hydroxylamine hydrochloride. Do not use this solution after one month.

2.11.2 Triturate 0.2 g of eriochrome black-T with 50 g of potassium chloride, in a glass mortar until the eriochrome black - T is evenly distributed.

3 APPARATUS

3.1 pH meter

3.2 Magnetic stirrer

4 PROCEDURE

4.1 Preparation of test solution

4.1.1 *Fertilizer containing little or no organic matter*

Weigh, to the nearest milligram, 2.5 g of the prepared test sample and transfer to a 400-ml beaker. Add carefully 50 ml of water and 5 ml of concentrated hydrochloric acid (2.1) (there may be a vigorous reaction due to carbon dioxide formation). Add more, concentrated hydrochloric acid (2.1) until effervescence is stopped. Evaporate to dryness on a steam bath, stirring occasionally with a glass rod. Continue the heating for at least one hour to dehydrate any silica which may be present. Add 10 ml of hydrochloric acid (2.2) and 20 ml of water. Stir with glass rod and cover the beaker with a watch glass. Boil the solution gently until dissolution is complete, and then filter through a fast filter paper into a 1000-ml volumetric flask. Wash the beaker and the filter once with 5 ml of hot hydrochloric acid (2.2) and twice with boiling water, collecting the washings in the flask. Cool and make up to the mark with water.

4.1.2 *Fertilizer containing organic matter*

Weigh, to the nearest milligram, 5 g of the prepared test sample into a silica or platinum crucible and place in a muffle furnace. Gradually raise the temperature to about 450 °C (not exceeding 475 °C) over a period of about one and half hours. Maintain at this temperature for at least 16 hours and then open the furnace and allow the crucible to cool. Moisten the ash and transfer it into a 250-ml beaker. Wash the crucible with about 5 ml of concentrated hydrochloric acid (2.1) and add slowly and carefully to the beaker (there may be a vigorous reaction due to carbon dioxide formation). Add more, concentrated hydrochloric acid (2.1) until effervescence is stopped. Evaporate to dryness on a steam bath, stirring occasionally with a glass rod. Continue the heating for at least one hour to dehydrate any silica which may be present. Add 10 ml of hydrochloric acid (2.2) and 20 ml of water. Stir with glass rod and cover the beaker with a watch glass. Boil the solution gently until dissolution is complete, and then filter through a fast filter paper into a 1000-ml volumetric flask. Wash the beaker and the filter once with 5 ml of hot hydrochloric acid (2.2) and twice with boiling water, collecting the washings in the flask. Cool and make up to the mark with water.

4.2 Standardization of EDTA solution

4.2.1 *Standardization with calcium standard solution*

Pipette 10 ml of the calcium standard solution (2.3) into a titration flask, add 100 ml of water and neutralise with ammonia solution (2.4) using litmus paper as the indicator. Add 10 ml of potassium hydroxide-potassium cyanide solution (2.5) and about 25 mg of HHSNNA indicator (2.6). Using a magnetic stirrer, titrate with 0.01 mol/l EDTA solution (2.7), until the colour changes permanently from wine red to pure blue. Titrate two more aliquots and calculate the average volume of EDTA solution required for the titration.

4.2.2 Standardization with magnesium standard solution

Pipette 10 ml of the magnesium standard solution (2.8) into a titration flask and add 100 ml of water. Add 5 ml of pH 10 buffer solution (2.9), 2 ml of potassium cyanide solution (2.10) and 10 drops of eriochrome black-T indicator solution (2.11.1) or 25 mg of powdered eriochrome black-T indicator (2.11.2). Using a magnetic stirrer, titrate with 0.01 mol/l EDTA solution (2.7), until the colour changes permanently from wine red to pure blue. Titrate two more aliquots and calculate the average volume of EDTA solution required for the titration.

4.3 Determination of calcium and magnesium

4.3.1 Calcium

Pipette 10 ml of the test solution (4.1.1 or 4.1.2) titrate with 0.01 mol/l EDTA solution (2.7) as given in (4.2.1).

4.3.2 Magnesium

Pipette 10 ml of the test solution (4.1.1 or 4.1.2) and titrate with 0.01 mol/l EDTA solution (2.7) as given in (4.2.2).

5 CALCULATION

5.1 Concentration of the EDTA solution

5.1.1 Concentration of the EDTA solution, in mol/l with respect to calcium standard solution (c_1) = $\frac{1}{4V_1}$

where,

V_1 is the volume in millilitres of EDTA solution required for the titration of 10 ml of the calcium standard solution.

5.1.2 Concentration of the EDTA solution, in mol/l with respect to magnesium standard solution (c_2) = $\frac{5}{12V_2}$

where,

V_2 is the volume in millilitres of EDTA solution required for the titration of 10 ml of the magnesium standard solution.

5.2 Determination of calcium content in the sample.

$$\text{Calcium content, as Ca, per cent by mass} = 400 \frac{V_3 - c_1}{m}$$

Where,

V_3 is the volume, in millilitres, of EDTA solution required for the titration of 10 ml of the sample solution with HHSNNA indicator;

c_1 is the concentration, in mol/l, of EDTA solution with respect to calcium standard solution; and

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

NOTE

Conversion factor, Ca to CaO is 1.4.

5.3 Determination of magnesium content in the sample

$$\text{Magnesium content, as Mg, per cent by mass} = 240 \frac{(V_4 - V_3) c_2}{m}$$

Where,

V_4 is the volume, in millilitres of the EDTA solution required for the titration of 10 ml of the sample solution with eriochrome black-T indicator;

c_2 is the concentration, in mol/l, of EDTA solution with respect to magnesium standard solution; and

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

NOTE

Conversion factor, Mg to MgO is 1.66.

SECTION 2 : DETERMINATION OF CALCIUM CONTENT - ATOMIC ABSORPTION SPECTROPHOTOMETRIC METHOD**1 PRINCIPLE**

The sample is ashed and dissolved in hydrochloric acid or, if it contains no organic substances, it is dissolved directly in hydrochloric acid. The solution is diluted and the calcium content of the extract is determined by atomic absorption spectrophotometry.

2 REAGENTS

Unless specified otherwise, reagents of analytical grade and distilled water or water of equivalent purity shall be used.

2.1 *Hydrochloric acid*, concentrated (rel.den. = 1.18)

2.2 *Hydrochloric acid*, 50 per cent (V/V) solution, prepared by using concentrated hydrochloric acid (rel.den. = 1.18).

2.3 *Calcium stock solution*

Dry, calcium carbonate at 105 °C for one hour. Weigh 2.497 g of the dried calcium carbonate and transfer to 1000- ml volumetric flask, using approximately 100 ml of water. Add slowly, while swirling, 60-ml of 1 mol/l solution of hydrochloric acid. When all the carbonate is dissolved, make up to the mark with water.

One millilitre of this solution contains 1 mg of calcium.

2.3.1 *Calcium working solution*

Dilute 20 ml of stock solution (2.3) to 200 ml.

One millilitre of this solution contains 0.1 mg of calcium.

2.4 *Lanthanum oxide solution (releasing agent)*

Moisten 117.3 g of lanthanum oxide (La_2O_3) low in calcium content. Add slowly 350 ml of concentrated hydrochloric acid (rel.den = 1.18) and stir until all the lanthanum oxide is dissolved. Allow to cool and transfer quantitatively into 1000-ml volumetric flask. Dilute up to the mark with water.

One millilitre of this solution contains 100 mg of lanthanum.

3 APPARATUS

Atomic absorption spectrophotometer with a calcium hollow cathode lamp.

4 PROCEDURE

4.1 Preparation of solutions

4.1.1 *Test solution*

4.1.1.1 Fertilizer containing little or no organic matter

Weigh, to the nearest milligram 2.5 g of the prepared test sample and transfer to a 400-ml beaker. Add carefully 50 ml of water and 5 ml of concentrated hydrochloric acid (2.1) (there may be a vigorous reaction due to carbon dioxide formation). Add more, concentrated hydrochloric acid (2.1) until effervescence is stopped. Evaporate to dryness on a steam bath, stirring occasionally with a glass rod. Continue the heating for at least one hour to dehydrate any silica which may be present. Add 10 ml of hydrochloric acid (2.2) and 20 ml of water. Stir with glass rod and cover the beaker with a watch glass. Boil the solution gently until dissolution is complete, and then filter through a fast filter paper into a 250-ml volumetric flask. Wash the beaker and the filter once with 5 ml of hot hydrochloric acid (2.2) and twice with boiling water, collecting the washings in the flask. Cool and make up to the mark with water.

4.1.1.2 Fertilizer containing organic matter

Weigh, to the nearest milligram, 5 g of the prepared test sample into a silica or a platinum crucible and place in a muffle furnace. Gradually raise the temperature to about 450 °C (not exceeding 475 °C) over a period of about one and half hours. Maintain at this temperature for at least 16 hours and then open the furnace and allow the crucible to cool. Moisten the ash and transfer it into a 250-ml beaker. Wash the crucible with about 5 ml of concentrated hydrochloric acid (2.1), and add slowly and carefully to the beaker (there may be vigorous reaction due to carbon dioxide formation). Add more, concentrated hydrochloric acid (2.1) until effervescence is stopped. Evaporate to dryness on a steam bath, stirring occasionally with a glass rod. Continue the heating for at least one hour to dehydrate any silica which may be present. Add 10 ml of hydrochloric acid (2.2) and 20 ml of water. Stir with glass rod and cover the beaker with a watch glass. Boil the solution gently until dissolution is complete, and then filter through a fast filter paper into a 250-ml volumetric flask. Wash the beaker and the filter once with 5 ml of hot hydrochloric acid (2.2) and twice with boiling water, collecting the washings in the flask. Cool and make up to the mark with water.

4.1.2 *Blank solution*

Prepare a blank solution omitting the sample.

4.1.3 *Dilute test and blank solutions*

Dilute, test solution (4.1.1.1 or 4.1.1.2) and the blank solution (4.1.2) to a concentration within the optimal measuring range of the spectrophotometer. Add sufficient releasing agent (2.4) to the diluted solutions to give a concentration of 10 per cent (V/V) of releasing agent in each solution.

4.1.4 *Standard solutions*

Dilute, the calcium working solution (2.3.1) to obtain at least five standard solutions of increasing concentration within the optimal measuring range of the spectrophotometer. Add sufficient releasing agent (2.4) to diluted solutions to give a concentration of 10 per cent (V/V) of releasing agent in each solution.

4.2 **Measurement**

Set the spectrophotometer using the line at a wave length of 422.7 nm. Use a fuel rich flame. Aspirate successively, in triplicate, the standard solutions (4.1.4), the diluted test solution and the blank solution (4.1.3) washing with water between each aspiration. Plot the calibration curve using the median absorbances of the standard solutions against concentrations of calcium. Determine the concentration of calcium in the test solution and the blank solution by reference to the calibration curve.

5 **CALCULATION**

calculate the percentage of calcium as Ca or CaO (see note) taking into account, the mass of the test sample, the dilution carried out in the course of the analysis and the results of the blank test.

NOTE

Conversion factor, Ca to CaO is 1.4.

SECTION 3 : DETERMINATION OF MAGNESIUM CONTENT - ATOMIC ABSORPTION SPECTROPHOTOMETRIC METHOD

1 PRINCIPLE

The sample is ashed and dissolved in dilute hydrochloric acid or, if it contains no organic substances, it is dissolved directly in dilute hydrochloric acid. The solution is diluted and the magnesium content of the extract is determined by atomic absorption spectrophotometry.

2 REAGENTS

Unless specified otherwise, reagents of analytical grade and distilled water or water of equivalent purity shall be used.

2.1 *Hydrochloric acid*, concentrated (rel.den. = 1.18)

2.2 *Hydrochloric acid*, 6 mol/l solution

2.3 *Hydrochloric acid*, 0.5 mol/l solution

2.4 **Magnesium solution**

Prepare the magnesium solution as given in (2.4.1) or (2.4.2).

2.4.1 Dissolve 1.013 g of magnesium sulfate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) in 0.5 mol/l solution of hydrochloric acid in 100 ml volumetric flask. Dilute up to the mark with the same hydrochloric acid.

One millilitre of this solution contains 1 mg of magnesium.

2.4.2 Dissolve 1.658 g of magnesium oxide, previously calcined at 600°C for 2 hours, in 120 ml of 1 mol/l solution of hydrochloric acid in a 100-ml volumetric flask. After dissolution is complete dilute up to the mark with water.

One millilitre of this solution contains 1 mg of magnesium.

2.5 **Releasing agent**

Prepare releasing agent as given in (2.5.1) or (2.5.2).

2.5.1 *Strontium chloride solution*

Dissolve 76.08 g of strontium chloride ($\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$) in 0.5 mol/l hydrochloric acid in 500-ml volumetric flask. Dilute up to the mark with the same acid.

One millilitre of this solution contains 50 mg of strontium.

2.5.2 *Lanthanum oxide solution*

Moisten 117.3 g of lanthanum oxide (La_2O_3), low in magnesium content. Add 350 ml of concentrated hydrochloric acid (rel. den. = 1.18) and stir until the lanthanum oxide is dissolved. Allow to cool and transfer quantitatively into a 1000-ml volumetric flask. Dilute up to the mark with water.

One millilitre of the solution contains 100 mg of lanthanum.

3 APPARATUS

Atomic absorption spectrophotometer with magnesium lamp.

4 PROCEDURE

4.1 Preparation of solutions

4.1.1 *Test solution*

4.1.1.1 Fertilizer containing little or no organic matter

Weigh, to the nearest milligram 2.5 g of the prepared test sample and transfer to a 400-ml beaker. Add carefully 50 ml of water and 5 ml of concentrated hydrochloric acid (2.1) (there may be a vigorous reaction due to carbon dioxide formation). Add more, concentrated hydrochloric acid (2.1) until effervescence is stopped. Evaporate to dryness on a steam bath stirring occasionally with a glass rod. Continue the heating for at least one hour to dehydrate any silica which may be present. Add 15 ml of hydrochloric acid (2.2) and 120 ml of water. Stir with glass rod and cover the beaker with a watch glass. Boil the solution gently until dissolution is complete, and then filter through a fast filter paper into a 250-ml volumetric flask. Wash the beaker and the filter once with 5 ml of hot hydrochloric acid (2.2) and twice with boiling water, collecting the washings in the flask. Cool and make up to the mark with water.

4.1.1.2 Fertilizer containing organic matter

Weigh, to the nearest milligram 5 g of the prepared test sample into a silica or platinum crucible and place in a muffle furnace. Gradually raise the temperature to 450 °C (not exceeding 475 °C) over a period of about one and half hours. Maintain at this temperature for at least 16 hours and then open the furnace and allow the crucible to cool. Moisten the ash and transfer it into a 250-ml beaker. Wash the crucible with about 5 ml of concentrated hydrochloric acid (2.1), add slowly and carefully to the beaker (there may be vigorous reaction due to carbon dioxide formation). Add more, concentrated hydrochloric acid (2.1) until effervescence is stopped. Evaporate to dryness on a steam bath stirring occasionally with a glass rod.

Continue the heating for at least one hour to dehydrate any silica which may be present. Add 15 ml of hydrochloric acid (2.2) and 120 ml of water. Stir with glass rod and cover the beaker with a watch glass. Boil the solution gently until dissolution is complete and then filter through a medium fast filter paper into a 250-ml volumetric flask. Wash the beaker and the filter once with 5 ml of hot hydrochloric acid (2.2) and twice with boiling water, collecting the washings in the flask. Cool and make up to the mark with water.

4.1.2 *Blank solution*

Prepare a blank solution omitting the sample.

4.1.3 *Dilute test and blank solutions*

Dilute, test solution (4.1.1.1 or 4.1.1.2) and the blank solution (4.1.2) with 0.5 mol/l hydrochloric acid (2.3) to a concentration within the optimal measuring range of the spectrophotometer. Add sufficient releasing agent (2.5.1 or 2.5.2) to the diluted solutions to give a concentration of 0.5 g of strontium or 1.0 g of lanthanum per 100 ml in each solution.

4.1.4 *Standard solutions*

Dilute, the magnesium solution (2.4.1 or 2.4.2) with 0,5 mol/l hydrochloric acid (2.3) to obtain at least five standard solutions of increasing concentration within the optimal measuring range of the spectrophotometer. Add sufficient releasing agent (2.5.1 or 2.5.2) to diluted solutions to give a conceatration of 0.5 g of strontium or 1.0 g of lanthanum per 100 ml in each solution.

4.2 **Measurement**

Set the spectrophotometer at a wave length of 285.2 nm using an oxidising air-acetylene flame. Aspirate successively, in triplicate the standard solutions (4.1.4), the dilute test solution and the blank solution (4.1.3), washing with water between each aspiration. Plot the calibration curve using the median absorbances of the standard solutions against concentrations of magnesium. Determine the concentration of magnesium in the test solution and the blank solution by reference to the calibration curve.

5 **CALCULATION**

Calculatre the pecentage of magnesium content of the sample as Mg or MgO (see note) taking into account, the mass of the test sample, the dilution carried out in the course of the analysis and the results of the blank test.

NOTE

Conversion factor, Mg to MgO is 1.66.

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SRI LANKA STANDARDS INSTITUTION

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The principal objects of the Institution as set out in the Act are to prepare standards and promote their adoption, to provide facilities for examination and testing of products, to operate a Certification Marks Scheme, to certify the quality of products meant for local consumption or exports and to promote standardization and quality control by educational, consultancy and research activity.

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