SLOVENSKI STANDARD
kSIST-TS FprCEN/TS 16198:2011

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Gnojila - Določevanje magnezija s kompleksometrijo

Fertilizers - Determination of magnesium by complexometry

Düngemittel - Komplexometrische Bestimmung von Magnesium

Engrais - Dosage du magnésium par complexométrie

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ICS:

65.080 Gnojila Fertilizers

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TECHNICAL SPECIFICATION

SPÉCIFICATION TECHNIQUE

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FINAL DRAFT
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ICS

English Version

Fertilizers - Determination of magnesium by complexometry

Engrais - Dosage du magnésium par complexométrie

Düngemittel - Komplexometrische Bestimmung von Magnesium

This draft Technical Specification is submitted to CEN members for formal vote. It has been drawn up by the Technical Committee CEN/TC 260.

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EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

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Contents

Page

Foreword

This document (FprCEN/TS 16198:2010) has been prepared by Technical Committee CEN/TC 260 “Fertilizers and liming materials”, the secretariat of which is held by DIN.

This document is currently submitted to the Formal Vote.

This document has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association.

1 Scope

This Technical Specification specifies a method for the determination of magnesium in fertilizer extracts.

The method is applicable to the following EC fertilizer extracts for which the determination of total magnesium and/or water-soluble magnesium is provided for according to the Regulation (EC) No 2003/2003, Annex I [1]:

— fertilizers listed in [1], Annex I: straight nitrogenous fertilizers, type 1b + 1c (calcium magnesium nitrate), type 7 (magnesium sulfonitrate), type 8 (nitrogenous fertilizers with magnesium) and straight potassic fertilizers, type 2 (enriched kainite), type 4 (potassium chloride containing magnesium), type 6 (potassium sulfate containing magnesium salt);

— fertilizers listed in [1], Annex I D relating to secondary nutrients.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 1482-2, *Fertilizers and liming materials — Sampling and sample preparation — Part 2: Sample preparation*

EN 12944-1:1999, *Fertilizers and liming materials and soil improvers — Vocabulary — Part 1: General terms*

EN 12944-2:1999, *Fertilizers and liming materials and soil improvers — Vocabulary — Part 2: Terms relating to fertilizers*

CEN/TS 15960, *Fertilizers — Extraction of total calcium, total magnesium, total sodium and total sulfur in the forms of sulfates*

CEN/TS 15961, *Fertilizers — Extraction of water soluble calcium, magnesium, sodium and sulfur in the form of sulfates*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in EN 12944-1:1999 and EN 12944-2:1999 apply.

4 Principle

The magnesium is solubilized according to CEN/TS 15960 or CEN/TS 15961. First titration: with EDTA of Ca and Mg in the presence of Eriochrome black-T. Second titration: with EDTA of Ca in the presence of calcein or of calcone carbonic acid. Determination of magnesium by difference.

5 Sampling

Sampling is not part of the method specified in this document. A recommended sampling method is given in EN 1482-1.

Sample preparation shall be carried out in accordance with EN 1482-2. Grinding of the laboratory sample is recommended for homogeneity reasons.

6 Reagents

6.1 Magnesium standard solution, c = 0,05 mol/l.

6.1.1 Dissolve 1,232 g of magnesium sulfate ($MgSO_4$ $7H_2O$) in the hydrochloric acid solution (6.11) and make up to 100 ml with the same acid,

or

6.1.2 Weigh 2,016 g of magnesium oxide, previously calcined to remove all traces of carbonation. Place it in a beaker with 100 ml of water.

Stir in approximately 120 ml of hydrochloric acid (6.12).

After dissolution, transfer quantitatively into a graduated 1 000 ml flask. Make up to volume and mix.

1 ml of these solutions should contain 2,216 mg of Mg (= 2,016 mg of MgO).

The laboratory is responsible for testing the strength of this standard solution.

6.2 EDTA solution, c = 0,05 mol/l.

Weigh 18,61 g of the dihydrated disodium salt of ethylenediaminetetraacetic (EDTA) ($C_{10}H_{14}N_2Na_2O_8,2H_2O$), place it in a beaker (7.4) and dissolve in 600 ml to 800 ml of water. Transfer the solution quantitatively into a graduated flask (7.3). Make up the volume and mix. Check this solution with the standard solution (6.1) by taking a sample of 20 ml of the latter and by titration according to the analytical procedure described in 9.2.

1 ml of the EDTA solution should correspond to 1,216 mg of Mg (= 2,016 mg of MgO) and to 2,004 mg of Ca (= 2,804 mg CaO) (see remarks 11.1 and 11.6).

6.3 Calcium standard solution, c = 0,05 mol/l.

Weigh 5,004 g of dry calcium carbonate. Place it in a beaker with 100 ml of water. Progressively stir in 120 ml of hydrochloric acid (6.12).

Bring to the boil in order to drive off the carbon dioxide, cool, transfer quantitatively into a graduated 1 l flask, make up the volume with water and mix. Check this solution against the EDTA solution (6.2) following analytical procedure (9.3). 1 ml of this solution should contain 2,004 mg of Ca (= 2,804 mg of CaO) and should correspond to 1 ml of the EDTA solution (6.2).

6.4 Calcein indicator.

Carefully mix in a mortar 1 g of calcein with 100 g of sodium chloride. Use 10 mg of this mixture. The indicator changes from green to orange. Titration shall be carried out until an orange is obtained which is free from green tinges.

6.5 Calcon carbonic acid indicator.

Dissolve 400 mg of calcon carbonic in 100 ml of methanol. This solution may only be kept for approximately four weeks. Use three drops of this solution. The indicator changes from red to blue. Titration shall be carried out until a blue is obtained which is free from red tinges.

6.6 Eriochrome black-T indicator.

Dissolve 300 mg of Eriochrome black-T in a mixture of 25 ml of propanol-1 and 15 ml of triethanolamine. This solution may only be kept for approximately four weeks. Use three drops of this solution. This indicator turns from red to blue and titration shall be carried out until a blue is obtained which is free from red tinges. It

changes colour only when magnesium is present. If necessary add 1 ml of the magnesium standard solution (6.1).

When both calcium and magnesium are present the EDTA first forms a complex with the calcium and then with the magnesium. In that case two elements are determined concurrently.

6.7 Potassium cyanide solution, aqueous solution of w(KCN) = 2 %.

SAFETY PRECAUTIONS — Do not pipette by mouth and see 11.7.

6.8 Solution of potassium hydroxide and potassium cyanide.

Dissolve 280 g of KOH and 66 g of KCN in water, make up the volume to 1 l and mix.

6.9 Buffer solution, pH = 10,5.

In a graduated flask (7.5), dissolve 33 g of ammonium chloride in 200 ml of water, add 250 ml of ammonia (ρ_{20} = 0,91 g/ml) make up the volume with water and mix. Check the pH of the solution regularly.

6.10 Diluted hydrochloric acid, one volume of hydrochloric acid (ρ_{20} = 1,18 g/ml) plus one volume of water.

6.11 Hydrochloric acid solution, approximately c = 0,5 mol/l.

6.12 Hydrochloric acid solution, approximately c = 1 mol/l.

6.13 Sodium hydroxide solution, c = 5 mol/l.

7 Apparatus

7.1 Magnetic or mechanical stirrer.

7.2 pH meter.

7.3 1 000 ml graduated flask.

7.4 1 000 ml beaker.

7.5 500 ml graduated flask.

7.6 400 ml beaker.

8 Preparation of the extraction solution

Prepare the extraction solution according to CEN/TS 15960 or CEN/TS 15961.

9 Procedure

9.1 Control test

Carry out a determination on aliquot parts of solutions (6.1 and 6.3) such that the Ca/Mg ratio is approximately equal to that of the solution to be analyzed. To this end take a ml of Mg standard solution (6.3) and (b-a) ml of standard solution (6.1), where a and b are the volumes, in millilitres, of the EDTA solution used in the two titrations performed on the solution to be analyzed. This procedure is correct only if the solutions of EDTA, calcium and magnesium are exactly equivalent. If this is not the case, it is necessary to make corrections.

9.2 Aliquot samples to be taken

The aliquot part will as far as possible contain between 9 mg and 18 mg of magnesium (= 15 mg to 30 mg of MgO).

9.3 Titration in the presence of Eriochrome black-T

Pipette an aliquot part (9.2) of the solution to be analyzed into a beaker (7.6). Neutralize the surplus acid with the sodium hydroxide solution (6.12) using the pH meter. Dilute with water to approximately 100 ml. Add 5 ml of the buffer solution (6.9). The pH measured shall be 10,5 ± 0,1. Add 2 ml of the potassium cyanide solution (6.7) and three drops of the Eriochrome black-T indicator (6.6). Titrate with the EDTA solution (6.2). Stir gently with the stirrer (7.1) (see 11.2, 11.3 and 11.4). Take b as the volume, in millilitres, of the EDTA solution (6.2).

9.4 Titration in the presence of calcein or of calcon carbonic acid

Pipette an aliquot part of the solution to be analyzed equal to that taken from the above titration (9.3) and place it in a beaker (7.6). Neutralize the surplus acid with the sodium hydroxide solution (6.13) using the pH meter. Dilute with water to about 100 ml. Add 10 ml of the KOH/KCN solution (6.8) and the indicator (6.4 or 6.5). Stir gently with the stirrer (7.1) titrate with the EDTA solution (6.2) (see 11.2, 11.3 and 11.4). Take a as the volume, in millilitres, of the EDTA solution (6.2).

10 Calculation and expression of the result

For the EEC fertilizers to which the method is applicable (5 g of fertilizer in 500 ml of extract), calculate the MgO content as a mass fraction, w_{MgO}, in percent of the fertilizer according to Equation (1).

$$w_{MgO} = \frac{(b-a)\times T}{M} \quad (1)$$

For the EEC fertilizers to which the method is applicable (5 g of fertilizer in 500 ml of extract), calculate the Mg content as a mass fraction, w_{Mg}, in percent of the fertilizer according to Equation (2).

$$w_{Mg} = \frac{(b-a)\times T'}{M} \quad (2)$$

where

a is the volume of the EDTA solution (6.2), in millilitres, used for the titration in the presence of calcein or calcon carbonic acid;

b is the volume of the EDTA solution (6.2), in millilitres, used for the titration in the presence of Eriochrome black-T;

M is the mass of the sample present in the aliquot part taken, in grams;

T is 0,201 6 × mol/l of the EDTA solution (6.2) 0,05;

T' is 0,121 6 × mol/l of the EDTA solution (6.2) 0,05.

11 Remarks

11.1 The stoechiometric EDTA-metal ratio in the complexometric analyses is always 1:1 whatever the valency of the metal and in spite of the fact that EDTA is quadrivalent. The EDTA titration solution and the standard solutions will therefore be molar and not normal.