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Liming materials — Determination of the calcium content and magnesium content — Complexometric method

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National foreword

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The UK participation in its preparation was entrusted to Technical Committee CII/37, Fertilisers and related chemicals.

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Liming materials - Determination of the calcium content and magnesium content - Complexometric method

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Kalkdünger - Bestimmung des Calcium- und Magnesiumgehaltes - Komplexometrisches Verfahren

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CEN-CENELEC Management Centre: Rue de la Science 23, B-1040 Brussels

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Contents

European foreword

This document (EN 12946:2023) has been prepared by Technical Committee CEN/TC 260 "Fertilizers and liming materials", the secretariat of which is held by DIN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by December 2023, and conflicting national standards shall be withdrawn at the latest by December 2023.

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This document supersedes EN 12946:2000 and EN 12946:2000/AC:2002.

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

The main changes compared to the previous edition are listed below:

a) Normative references updated and added;

b) Reference to EN 12944-3 added in Clause 3;

c) Principle (Clause 4) updated to recognize the possibility to use automatic titration;

d) Reference updated in Clause 7;

e) Bibliography updated.

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Introduction

The complexometric method for the determination of calcium content and magnesium content in liming materials is based on a method, which is described in VDLUFA, Manual II of analysing methods for fertilizers [1].

1 Scope

This document specifies a complexometric method for the determination of the calcium content and the magnesium content of liming materials.

It is not applicable to products with a mass fraction less than 2 % magnesium or those with a mass fraction more than 1 % P_2O_5 and is not applicable to silicate liming materials.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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 1482-1, *Fertilizers and liming materials - Sampling and sample preparation - Part 1: Sampling*

EN 1482-3, *Fertilizers and liming materials - Sampling and sample preparation - Part 3: Sampling of static heaps*

EN 12944-3, *Fertilizers and liming materials - Vocabulary - Part 3: Terms relating to liming materials*

ISO 3310-1, *Test sieves — Technical requirements and testing — Part 1: Test sieves of metal wire cloth*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in EN 12944-3 apply.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

— IEC Electropedia: available at https://www.electropedia.org/

— ISO Online browsing platform: available at https://www.iso.org/obp

4 Principle

A test portion is extracted with boiling hydrochloric acid solution. After filtration and dilution, an aliquot portion is titrated against EDTA solution with calcein/thymolphthalein or calcon carbonic acid as indicator in order to measure calcium. A second aliquot portion is titrated against EDTA with eriochrome black T as indicator in order to measure calcium and magnesium.

This method can be performed manually or alternatively by means of an automatic titrator as far as equivalence is proved.

5 Reagents

5.1 General

In principle, commercially available standard solutions may be used instead of standard solutions produced on-site in the laboratory. Variations in concentration shall be taken into account for the calculation of the results.

5.2 Hydrochloric acid solution

Density at 20 °C ρ_{20} = 1,09 g/ml

Add 1 part by volume of hydrochloric acid (ρ_{20} = 1,18 g/ml) to 1 part by volume of water.

5.3 Hydrochloric acid solution

Substance concentration c(HCl) = 1 mol/l approximately.

5.4 Hydrochloric acid solution

c(HCl) = 0,5 mol/l approximately.

5.5 Standard calcium solution, containing 2,004 g of calcium per litre

Weigh 5,004 g of dry calcium carbonate into a 500 ml beaker and add 100 ml of water.

Under continuous stirring, slowly add 120 ml of hydrochloric acid solution (5.3).

Drive off the carbon dioxide by boiling, cool and transfer the solution quantitatively into a 1 000 ml volumetric flask and dilute to the mark with water.

Check the standard strength of the solution by titration with the EDTA standard solution (5.7) according to 8.3.

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 standard solution (5.7).

5.6 Standard magnesium solution, containing 1,216 g of magnesium per litre

5.6.1 Weigh 1,232 g of magnesium sulfate ($MgSO_4 \cdot 7H_2O$) into a 100 ml volumetric flask, dissolve in hydrochloric acid solution (5.4) and dilute to the mark with the same solution.

or

5.6.2 Calcined magnesium oxide (MgO) at 600 °C for 2 h.

Weigh 2,016 g of the freshly calcined MgO into a 500 ml beaker, dissolve in 100 ml of water and 120 ml of hydrochloric acid solution (5.3). Transfer the solution into a 1 000 ml volumetric flask and dilute to the mark with water.

1 ml of this solution should contain 1,216 mg Mg (2,016 mg of MgO/ml).

Before use check the Mg content of each standard solution after preparation.

5.7 Ethylenediamine tetraacetic acid (EDTA) standard solution, c(EDTA) = 0,05 mol/l

Weigh 18,61 g of ethylenediamine tetraacetic acid dihydrate disodium salt (EDTA; $C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$) into a 1 000 ml volumetric flask and dilute to the mark with water.

Check the standard strength of the solution by titration of 20 ml of the standard solution 5.6 according to 8.2.2.

1 ml of the EDTA standard solution should correspond to 1,216 mg of Mg or 2,016 mg of MgO and to 2,004 mg of Ca or 2,804 mg of CaO.

NOTE The stoichiometric EDTA/metal ion-ration is always 1:1 whatever the valency of the determination metal ion is.

5.8 Calcein thymolphthalein indicator

Carefully mix 0,2 g of calcein with 0,12 g thymolphthalein and 20 g of potassium nitrate in a mortar. Use 10 mg of this mixture for each titration. The indicator changes from green to orange.

Titration shall be carried out until an orange is obtained which is free from green tinges.

5.9 Calcon carbonic acid indicator

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

5.10 Eriochrome black T indicator

Dissolve 300 mg of eriochrome black T in a mixture of 25 ml of propan-1-ol and 15 ml of triethanolamine. This solution may only be kept for approximately four weeks. Use three drops of this solution. This indicator changes its colour from red to blue and titration shall be carried out until a blue colour is obtained which is free from red tinges. It changes colour only when magnesium is present. If necessary add 1 ml of the standard solution (5.6).

5.11 Triethanolamine

Aqueous solution of triethanolamine with a mass fraction of 50 %.

5.12 Buffer solution, pH 10,5

Dissolve 33 g of ammonium chloride in 100 ml of water in a 500 ml volumetric flask, add 250 ml of concentrated ammonia solution (ρ_{20} = 0,92 g/ml; about a mass fraction of 25 % NH_3 solution) and dilute to the mark with water.

5.13 Sodium hydroxide solution

c(NaOH) = 5 mol/l

6 Apparatus

Usual laboratory apparatus and in particular the following:

6.1 Test sieve conforming to the requirements of ISO 3310-1, of nominal aperture size 250 µm.

6.2 Pestle and mortar, each of porcelain, or mechanical grinder.

6.3 Electric hot plate with adjustable temperature.

6.4 Magnetic or mechanical stirrer.

6.5 pH meter, minimum sensitivity 0,05 units with suitable electrodes, calibrated using two suitable buffer solutions.

7 Sampling

Sampling of liming materials shall be in accordance with EN 1482-1 or EN 1482-3.

8 Procedure

8.1 Preparation

8.1.1 Preparation of test sample

Prepare the received laboratory sample by grinding (6.2) and sieving it rapidly through the test sieve (6.1).

Grind the sample to pass the 250 µm sieve.

Mix the test sample thoroughly.

NOTE EN 1482-2 describes sample preparation.

8.1.2 Preparation of test solution

Weigh about 1 g to the nearest 0,001 g of the test sample into a 600 ml beaker and add approximately 400 ml of water. Carefully add 50 ml of hydrochloric acid solution (5.2) and boil for 30 min. Allow to cool to ambient temperature under stirring.

Transfer the solution quantitatively to a 500 ml volumetric flask, dilute to the mark with water and mix.

Filter through a dry filter, discarding the first 50 ml of the filtrate. The solution shall be clear without any turbidity.

Store this test solution in a stoppered flask, if the determination is not carried out immediately afterwards.

8.2 Determination

8.2.1 Aliquot portion

Take an aliquot portion, expected to contain between 15 mg and 30 mg of calcium and between 9 mg and 18 mg of magnesium of the test solution (8.1.2).

8.2.2 Titration in the presence of eriochrome black T

Pipette the aliquot portion (8.2.1) into a 400 ml beaker. Neutralize the surplus acid with the sodium hydroxide solution (5.13) using the pH meter. Dilute with water to approximately 100 ml. Add 5 ml of the buffer solution (5.12). The pH should be 10,5 ± 0,1. Add 5 ml Triethanolamine (5.11) and three drops of the eriochrome black T indicator (5.10). Stir gently with the stirrer (6.4) and titrate with the EDTA standard solution (5.7).

In particular the eriochrome T-magnesium complex is often relatively stable. Therefore, it can take some time for the change in colour at the final point of titration. For that reason, it is important to operate the titration very carefully. Check the final point of titration with a drop of standard magnesium solution (5.6) or standard calcium solution (5.5).

Observe the colour of the solution from horizontal position at the end of the titration. Place the beaker with the titration solution well lit in front of a white coloured background. The observation of the change in colour can also be facilitated by placing the beaker on frosted glass lighted moderately from below (e.g. with a 25 W lamp).

NOTE 1 The use of triethanolamine is not required for products with a low content of impurities (e.g. iron).

NOTE 2 In particular, the eriochrome black T indicator and the calcon carbonic acid indicator are often sensitive to oxidation by air. Therefore, the solution can lose colour during titration. If this occurs, the correct course of action is to add one or two drops of the corresponding indicator solution.

8.2.3 Titration in the presence of calcein thymolphthalein or calcon carbonic acid

Pipette the aliquot portion (8.2.1) into a 400 ml beaker. Neutralize the surplus acid with the sodium hydroxide solution (5.13) using the pH meter and adjust the pH value to 13,0. The pH value shall not fall below this value during titration. Dilute with water to about 100 ml. Add 5 ml Triethanolamine (5.11) and the indicator (5.8) or (5.9). Stir gently with the stirrer (6.4) and titrate with the EDTA standard solution (5.7) (see Notes 1 to 2 in 8.2.2).

8.3 Control test of the standard solutions

Carry out a determination on aliquot parts of solutions (5.5 and 5.6) such that the Ca/Mg ratio is approximately equal to that of the test solution to be analysed. For this test take (a) ml of the standard calcium solution (5.5) and (b-a) ml of the standard magnesium solution (5.6), where (a) and (b) are the volumes (in ml) of EDTA solution used in the two titrations of the test solution described in 8.2.3 and 8.2.2 respectively.

This procedure is correct only if the standard solutions of EDTA, calcium and magnesium are exactly equivalent. If this is not the case, it is necessary to make the appropriate corrections.

9 Expression of results

The calcium content w_{Ca} and the magnesium content w_{Mg}, expressed as a percentage by mass, is given by the following equations:

$$w_{\mathrm{Ca}} = \frac{V_1 \times T_1}{m} \quad (1)$$

$$w_{\mathrm{Mg}} = \frac{\left(V_2 - V_1\right) \times T_2}{m} \quad (2)$$

where

m is the mass of sample contained in the aliquot portion (8.2.1), in g;

V_1 is the volume of EDTA standard solution used for the titration in the presence of calcein/thymolphthalein or calcon carbonic acid, in ml;

V_2 is the volume of EDTA standard solution used for the titration in the presence of eriochrome black T, in ml;

$T_{1\mathrm{Ca}}$ 0,2004 × correction factor $K_{\mathrm{c(EDTA)}}$ of the EDTA standard solution, in g/l (according to 5.7);

$T_{2\mathrm{Mg}}$ 0,1216 × correction factor $K_{\mathrm{c(EDTA)}}$ of the EDTA standard solution, in g/l (according to 5.7).

To calculate the calcium content expressed as CaO and the magnesium content expressed as MgO use the following factors:

$T_{1\mathrm{CaO}}$ 0,2804 × correction factor $K_{\mathrm{c(EDTA)}}$ of the EDTA standard solution, in g/l (according to 5.7);

$T_{2\mathrm{MgO}}$ 0,2016 × correction factor $K_{\mathrm{c(EDTA)}}$ of the EDTA standard solution, in g/l (according to 5.7).

10 Precision

10.1 General

The values derived from inter-laboratory tests with building lime products in accordance with EN 459-2.

10.2 Repeatability

The absolute difference between two single test results found on identical test material by one operator using the same apparatus within the shortest feasible time interval will exceed the repeatability limit r in not more than 5 % of cases.

The values are:

s_r = 0,15 % mass fraction for Ca

and

s_r = 0,21 % mass fraction for Mg

NOTE s_r is the repeatability standard deviation.

10.3 Reproducibility

The absolute difference between two single test results on identical test material reported by two laboratories will exceed the reproducibility limit R in not more than 5 % of the cases.

The values are:

s_R = 0,43 % mass fraction for Ca

and

s_R = 0,25 % mass fraction for Mg

NOTE s_R is the reproducibility standard deviation.

11 Test report

The test report shall contain at least the following information:

a) all data necessary for the identification of the sample;

b) a reference to this document (including its year of publication);

c) the results and the units in which the results have been expressed;

d) the date of the test;

e) any particular points observed in the course of the test;

f) any operations not specified in the method or regarded as optional which can have affected the results.

Bibliography

[1] VDLUFA, Manual II of analyzing methods for fertilizers. VDLUFA-Verlag, c/o LUFA Speyer, Obere Langgasse 40, Speyer

[2] Regulation (EU) 2019/1009 of the European Parliament and of the Council of 5 June 2019 laying down rules on the making available on the market of EU fertilising products and amending Regulations (EC) No 1069/2009 and (EC) No 1107/2009 and repealing Regulation (EC) No 2003/2003

[3] EN 459-2, *Building lime - Part 2: Test methods*

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

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BSI Group Headquarters

389 Chiswick High Road London W4 4AL UK

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