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Liming materials — Determination of neutralizing value — Titrimetric methods

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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.

A list of organizations represented on this committee can be obtained on request to its secretary.

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Liming materials - Determination of neutralizing value - Titrimetric methods

Amendements minéraux basiques - Détermination de la valeur neutralisante - Méthodes par titrimétrie

Kalkdünger - Bestimmung des Neutralisationswertes - Titrimetrische Verfahren

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Foreword

This document (EN 12945:2014) 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of an identical text or by endorsement, at the latest by October 2014 and conflicting national standards shall be withdrawn at the latest by October 2014.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN [and/or CENELEC] shall not be held responsible for identifying any or all such patent rights.

This document supersedes EN 12945:2008.

The following changes have been made to the former edition:

a) scope modified taking into account that method A is not applicable to liming materials with more than 3 % P_2O_5 and that method B is applicable to all liming materials;

b) reference to EN 14984 added to the scope and the Bibliography;

c) 9.2 amended by addition of an instruction concerning the use of correction factors;

d) optional requirement concerning correction factors added to Clause 11 Test report;

e) corrigendum EN 12945:2008/AC:2009 included;

f) editorially revised.

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Introduction

Two different procedures are described (method A and method B) because the titration to pH 7,0 is not applicable to silicate liming materials due to the precipitation of compounds at this pH value.

In method B the turning point at pH 4,8 on the titration curve is taken as the end-point of the titration. For carbonaceous liming materials the difference in the consumption of sodium hydroxide solution for back titration between the titration end-points of pH 4,8 and pH 7,0 is negligible.

1 Scope

This European Standard specifies two methods for the determination of the neutralizing value (NV) of liming materials.

Method A is applicable to all liming materials except silicate liming materials.

Method B is applicable to all liming materials.

Both methods do not correctly take into account the potential neutralizing value of material containing more than 3 % P_2O_5. For a more accurate agronomic assessment of products containing more than 3 % P_2O_5 determine the liming efficiency according to EN 14984.

NOTE The methods described in ISO 6598 [1] and ISO 7497 [2] can be used for the determination of P_2O_5 content. Further information on P analyses is given in [3] and [4].

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. 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 12944-3:2001, *Fertilizers and liming materials —Vocabulary — Part 3: Terms relating to liming materials*

EN ISO 3696, *Water for analytical laboratory use — Specification and test methods (ISO 3696)*

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 12944-3:2001 apply.

4 Principle

Dissolution of the sample in a specified quantity of hydrochloric acid standard solution. Determination of the excess acid by back titration with a sodium hydroxide standard solution.

5 Reagents

During the analysis, unless otherwise stated, use only reagents of recognised analytical grade.

NOTE Commercially available solutions can be used.

5.1 Water, according to EN ISO 3696, grade 3.

5.2 Hydrochloric acid standard solution, c(HCl) = 0,5 mol/l.

Determine the exact concentration of the solution by titration with sodium hydroxide standard solution (5.3) using phenolphthalein solution (5.4) as indicator. Apply the appropriate correction factor in the calculation of the results (see Clause 9).

5.3 Sodium hydroxide standard solution, c(NaOH) = 0,25 mol/l.

Determine the exact concentration of the standard solution by titration against approximately 2 g of dried potassium hydrogen phthalate ($KHC_8H_4O_4$), weighed to the nearest 0,001 g.

The solution shall be stored in a polyethylene bottle and absorption of carbon dioxide during storage should be avoided.

NOTE 1 ml of 0,25 mol/l sodium hydroxide solution is equivalent to 51,055 mg of potassium hydrogen phthalate.

Apply the appropriate correction factor in the calculation of the results (see Clause 9).

5.4 Phenolphthalein indicator solution.

Dissolve 0,25 g of phenolphthalein in 150 ml of ethanol with a mass fraction of 93 % and dilute with water to 250 ml.

Use the phenolphthalein solution (5.4) as an indicator.

5.5 Hydrogen peroxide solution.

Dilute one volume of hydrogen peroxide [ρ (H_2O_2) = 30 g/100 ml] with four volumes of water.

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 pH meter, minimum sensitivity 0,05 pH units, with a suitable glass electrode and a calomel or other reference electrode or a combined electrode, calibrated using two buffer solutions whose pH values cover the range pH 4 to pH 7.

6.3 Mechanical stirrer, e.g. magnetic stirrer.

6.4 Desiccator.

7 Sampling

Sampling is not part of the method specified in this European Standard. A recommended sampling method is described in EN 1482-1 [5].

Prepare the sample of the liming materials in accordance with EN 1482-2.

8 Procedure

8.1 Preparation of the test sample

Dry the test sample at (105 ± 2) °C to constant mass. Record the as-received (m_w) and dry (m_d) masses. Grind the sample so that it passes the 250 µm test sieve (6.1). Mix thoroughly and store the sample in a desiccator (6.4).

8.2 Determination

8.2.1 Method A

8.2.1.1 Test portion

Weigh about 0,5 g, to the nearest 0,001 g, of burnt or hydrated lime or 1 g of ground limestone or ground marl (prepared according to 8.1) into a 250 ml conical flask.

8.2.1.2 Titration

Add 50 ml of the hydrochloric acid standard solution (5.2) with continuous shaking and boil gently for 10 min, using boiling granules.

Cool to ambient temperature. Transfer quantitatively into a 250 ml beaker and insert the electrodes of the pH meter (6.2) and a stirrer (6.3).

Titrate with the sodium hydroxide standard solution (5.3) with moderate stirring (avoid splashing) until a pH of 7,0 is stable for 1 min whilst stirring is maintained.

8.2.2 Method B

8.2.2.1 Test portion

Weigh about 0,5 g, to the nearest 0,001 g, of the prepared test sample (8.1) into a 250 ml conical flask.

8.2.2.2 Titration

Rinse the inside walls of the flask with 10 ml of water.

Add 35 ml of the hydrochloric acid standard solution (5.2) with continuous shaking.

Heat and boil gently for 10 min to dissolve the sample using boiling granules. Stir continuously. Cool to ambient temperature, then dilute with water to about 100 ml and add 5 ml of hydrogen peroxide solution (5.5).

NOTE Ferrous ions in silicate liming materials are oxidized by hydrogen peroxide to ferric ions before titration, because ferrous ions otherwise would consume hydrogen ions during titration.

Transfer quantitatively into a 200 ml graduated flask; make up the volume with water and mix. Pass through a dry filter into a dry container, discarding the initial portion. Pipette an aliquot portion of 100 ml of the solution into a 250 ml beaker.

Insert the electrodes of the pH meter (6.2) and a stirrer (6.3).

Titrate with the sodium hydroxide standard solution (5.3) with moderate stirring (avoid splashing) until a pH of 4,8 is stable for 1 min (whilst stirring is maintained).

9 Calculation and expression of results for method A and method B

9.1 Calculate the neutralizing value of the dried product, N_d, according to Formula (1)

$$N_d = \frac{0{,}028 \times (M_1 \times V_1 \times f_1 \times A - M_2 \times V_2 \times f_2) \times 100}{m_t \times A} \quad (1)$$

where

0,028 is the factor to convert hydrochloric acid standard solution into CaO;

M_1 is the molarity of hydrochloric acid standard solution (5.2), in mol/l;

V_1 is the total volume of hydrochloric acid standard solution (5.2), in millilitres;

f_1 is the factor of hydrochloric acid standard solution (5.2);

A is equal to 1 for method A, and the factor of the taken aliquot is 0,5 for method B;

M_2 is the molarity of sodium hydroxide standard solution (5.3), in mol/l;

V_2 is the volume of sodium hydroxide standard solution (5.3), in millilitres;

f_2 is the factor of sodium hydroxide standard solution (5.3);

m_t is the mass of the test portion in the aliquot portion taken, in grams.

9.2 Calculate the neutralizing value of the “as-received” product, N_{ar}, according to Formula (2)

$$N_{ar} = \frac{N_d \, m_d}{m_w} \quad (2)$$

where

N_d is the neutralizing value of the dried sample;

m_d is the mass of the sample after drying, in grams;

m_w is the mass of the sample before drying, in grams.

The result shall be taken as the arithmetic mean of at least two determinations.

Expressions of results do not contain any correction factors to take into account material with a content of P_2O_5 greater than 3 %.

10 Precision

10.1 General

The precision of the method was established by an inter-laboratory trial carried out in 1999 in accordance with ISO 5725:1994 [6].

The values obtained for repeatability limit and reproducibility limit are expressed for the 95 % probability level are not applicable to concentration ranges and matrices other than those given.

NOTE The repeatability limits and reproducibility limits obtained from the inter-laboratory trial for each product being tested are given in Annex A.

10.2 Repeatability

The absolute difference between two independent single test results, obtained using the same method on identical test material in the same laboratory by the same operator using the same equipment within the shortest feasible time interval will exceed the repeatability limit (r) on average not more than once in 20 cases in the normal and correct operation of the method.

The value is:

r = 2,30 % (relative) at a mean mass fraction of 53 % CaO.

10.3 Reproducibility

The absolute difference between two independent single test results, obtained using the same method on identical test material in different laboratories with different operators using different equipment will exceed the reproducibility limit (R) on average not more than once in 20 cases in the normal and correct operation of the method.

The value is:

R = 12,64 % (relative) at a mean mass fraction of 53 % CaO.

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 European Standard, i.e. EN 12945;

c) the method used (method A or method B);

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

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

f) optionally a statement that correction factors for materials containing more than 3 % P_2O_5 are not included;

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

Annex A
(informative)
Results of an inter-laboratory trial to determine the neutralizing value

An inter-laboratory trial was organised in 1999 under the auspices of the European Committee for Standardization to obtain precision data for the method specified in this European Standard.

In these trial eight laboratories from five participating countries determined the neutralizing value of five types of product. The values derived from this inter-laboratory trial for the repeatability limit and reproducibility limit of each product being tested are given in Table A.1.

Table A.1 — Repeatability limits and reproducibility limits derived from inter-laboratory trial

Product type	**Mass fraction CaO** %	**Repeatability limit *r*** % relative	**Reproducibility limit *R*** % relative
Magnesium limestone, coarse	51,4	3,22	12,69
Dolomite, fine	58,9	1,58	5,51
Dolomite, coarse	55,6	2,25	11,46
Chalk, coarse	48,6	2,80	22,3
Blast furnace slag	50,8	1,62	11,17

Bibliography

[1] ISO 6598, *Fertilizers — Determination of phosphorus content — Quinoline phosphomolybdate gravimetric method*

[2] ISO 7497, *Fertilizers — Extraction of phosphates soluble in mineral acids*

[3] 77/535/EEC, *Commission Directive of 22 June 1977 on the approximation of the laws of the Member States relating to methods of sampling and analysis for fertilizers*, Annex II -Methods 3.1.1/3.2 Total phosphorus soluble in mineral acid. OJ EEC, 1977, N° L 213, p.62, 74-77

[4] *VDLUFA, Manual II of analyzing methods for fertilizers*, 12.3. (VDLUFA-Verlag, Bismarckstraße 41 A, D-64293 Darmstadt)

[5] EN 1482-1, *Fertilizers and liming materials - Sampling and sample preparation - Part 1: Sampling*

[6] ISO 5725 (all parts):1994, *Accuracy (trueness and precision) of measurement methods and results*

[7] EN 14984, *Liming materials - Determination of product effect on soil pH - Soil incubation method*

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