SLOVENSKI STANDARD
SIST EN 16357:2013

01-oktober-2013

Karbonatna sredstva za apnjenje - Določevanje reaktivnosti - Metoda avtomatske titracije s citronsko kislino

Carbonate liming materials - Determination of reactivity - Automatic titration method with citric acid

Carbonatische Kalke - Bestimmung der Reaktivität - Automatisches Titrationsverfahren mit Citronensäure

Amendements minéraux basiques carbonatés - Détermination de la réactivité - Méthode par titration automatique à l'acide citrique

Ta slovenski standard je istoveten z: **EN 16357:2013**

ICS:

65.080	Gnojila	Fertilizers

SIST EN 16357:2013 **en,fr,de**

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN 16357

August 2013

ICS 65.080

English Version

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COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

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Ref. No. EN 16357:2013: E

Contents

Page

Foreword

This document (EN 16357:2013) 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of an identical text or by endorsement, at the latest by February 2014, and conflicting national standards shall be withdrawn at the latest by February 2014.

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Introduction

This method has been prepared to improve existing agricultural reactivity methods (see [1], [2], [3], [4] and [5]) for carbonate liming materials: duration, accuracy, representativeness, closer from soil conditions, automation.

Attention is drawn to the following critical steps:

— identification of the liming material type (influence on precision data);

— size distribution (influence on test portion preparation and amount);

— calibration of pH electrode (influence on titrator's pH adjustments);

— pH stat programme setting (influence on accuracy of added amounts of citric acid solution);

— suitability of PCC used to check calibration;

— stirring device (provides homogeneousness without grinding);

— additional uncertainty with neutralising value and MgO content determination.

1 Scope

This European Standard specifies a method for the determination of the reactivity of calcium carbonate and calcium magnesium carbonate liming materials. It assesses the speed and effectiveness of their neutralising potential by automatic titration with citric acid.

This method is applicable only to liming materials with a maximum particle size of 6,3 mm determined according to EN 12948.

NOTE For marble dolomite (BET procedure according to ISO 9277 below 500 m^2/kg), see EN 14984.

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 12048, *Solid fertilizers and liming materials — Determination of moisture content — Gravimetric method by drying at (105 +/- 2) °C (ISO 8190, modified)*

EN 12945, *Liming materials — Determination of neutralizing value — Titrimetric methods*

EN 12948, *Liming materials — Determination of size distribution by dry and wet sieving*

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

3 Principle

Limited decomposition of carbonates in a given time with acid according to the following reaction:

$$MeCO_3 + 2H^+ \rightarrow Me^{2+} + H_2O + CO_2$$

Titration under stable pH conditions (pH 4,5) with an automatic titration apparatus. The citric acid consumption during a given time (15 min) is a direct measure for the reaction of the liming materials being tested.

4 Apparatus

Usual laboratory apparatus and, in particular, the following:

4.1 pH meter with electrode.

This instrument is generally included in the automatic motor driven burette device.

4.2 Automatic motor driven burette, capacity 20 ml.

This kind of burette is generally equipped with all necessary accessories such as pH regulation programme (pH stat), automatic refilling device, pH electrode, continuous pH measurement and propeller stirring device.

Though a propeller stirring device is preferred, a magnetic stirring device (4.7) may be used, provided the central ring of the stirrer rod is thick enough and does not lead to grind the tested material. Make sure the rotation speed of the stirrer rod is fast enough to make homogeneous dispersion in the beaker. If not, increase the speed up to the necessary value.

The burette shall be able to deliver at least 0,05 ml of citric acid solution (5.3) per second. This is to ensure the first part of the reaction (pH dropping from initial pH value to target pH value (4,5) will not be a limiting factor for liming material dissolution speed). This figure is higher than the flow rate obtained with the fastest reaction observed in preliminary tests.

The burette shall be able to deliver its whole content in at least 4 000 steps to ensure accuracy for low amount of citric acid solution (5.3).

NOTE This condition is always fulfilled with modern titrators. All contemporary (less than 10 years old) titrators allow such accuracy: i.e. minimum step amount: 0,002 5 ml for a 10 ml burette, or 0,012 5 ml for a 50 ml burette. This is sufficient, even for low amounts. However, this accuracy is obtained only if correct (minimal) step volume in titrator setup is specified. If not, the precision of the method will be altered.

Use the burette only for the citric acid solution (5.3).

For liming materials coarser than 1 mm, use a 50 ml burette.

For most of products, a 10 ml burette is sufficient. However, a 20 ml burette is necessary for highly reactive chalks and precipitated calcium carbonate. Because refilling takes a significant time, this can bias the results. If volumes higher than 10 ml are expected, do not use the automatic refilling possibility and use a 20 ml or a 50 ml burette.

4.3 Glass beaker, capacity 100 ml.

For liming materials coarser than 1 mm, use a 200 ml beaker.

Minimum diameter in case of magnetic stirring device (4.7): 50 mm.

4.4 Stop-watch.

4.5 Balance, capable of weighing 10 g to the nearest 0,01 g.

4.6 Sample changer, optional.

If occurring, a beaker of water (5.1) shall be inserted between two samples.

4.7 Magnetic stirring device, optional, see 4.2.

Capable of minimum 500 min^{-1} speed rotation.

Stirrer rod minimum length: 40 mm.

5 Reagents

All reagents shall be of recognised analytical grade.

5.1 Water, according to EN ISO 3696, grade 2.

5.2 Mono hydrated citric acid, $C_6H_8O_7$ H_2O, crystallised or powder, molar mass: 210,14 g.

Do not use anhydrous citric acid having a different molar mass, which can partially hydrate when storing.

5.3 Citric acid solution, ρ = 457,17 g/l.

Preferably, use a fresh home-made solution as described below. Under these conditions, the solution concentration is conventionally supposed to be equal to the necessary one, ρ_{ca} = 457,17 g pure citric acid per litre.

The solution may be used for up to, at most, one month stored in a closed, dark glass vessel. If the solution has been stored more than one week, check its concentration by any means, for example by titration with a strong base (NaOH) solution of known concentration and report the result in the formula given in Clause 8.

Weigh 500 g of mono hydrated citric acid (5.2) to the nearest 0,1 g. Pour it quantitatively into a 1 l measuring vessel. Rinse the weighing material and pour the rinsing water into the vessel in a way that it takes any acid stuck on the edge or on the bottom. Add about 500 ml of water (5.1) to the measuring vessel. Heat the vessel until full dissolution (temperature about 80 °C). Let the vessel cool to ambient temperature. Make up to the volume with water to 1 l. Stir to get a homogeneous solution.

The pure citric acid content, ρ_{ca}, ($C_6H_8O_7$), in grams per litre of this solution is calculated according to Formula (1) as follows.

$$\rho_{ca} = \frac{500 \times 192,14}{210,14} = 457,17 \qquad (1)$$

where

500 is the added mass of mono hydrated citric acid (5.2), in grams;

192,14 is the molar mass of anhydrous citric acid, in grams;

210,14 is the molar mass of mono hydrated citric acid, in grams.

5.4 Calcium carbonate, precipitated (or PCC), mass fraction, $w(CaCO_3)$ at least 99 %.

Commercial PCC for analysis is granted for its chemical characteristics. However, physical characteristics are not granted. As reactivity depends on fineness, even for PCC, it is essential to take as a reference a highly reactive PCC, such as commercial PCC from VWR / Prolabo / BDH, reference GPR, Rectapur, Ref 22296.294, Molar mass 100,09 [1], which will consume 15 ml after 15 min. This PCC was used in the ring test before launching measurements. By experience, some PCC do not meet this requirement. See also the note in 7.2.6.

5.5 Silicone defoamer.

5.6 Standard buffer solution, pH 4 (commercial solution, pH 4,01).

NOTE This solution has a limited lifetime.

5.7 Standard buffer solution, pH 7 (commercial solution, pH 6,98).

NOTE This solution has a limited lifetime.

6 Sampling and sample preparation

6.1 General

Sampling is not part of the methods 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.

1) This substance is an example of a suitable product available commercially. This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of this product.