SIST

SLOVENSKI STANDARD
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Karbonatna in silikatna sredstva za apnjenje - Določevanje reaktivnosti - Potenciometrijska titracijska metoda s klorovodikovo kislino

Carbonate and silicate liming materials - Determination of reactivity - Potentiometric titration method with hydrochloric acid

Carbonatische und silikatische Kalke - Bestimmung der Reaktivität - Potentiometrisches Titrationsverfahren mit Salzsäure

Amendements minéraux basiques carbonatés et silicatés - Détermination de la réactivité - Méthode par titrage potentiométrique à l'acide chlorhydrique

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Carbonate and silicate liming materials - Determination of reactivity - Potentiometric titration method with hydrochloric acid

Amendements minéraux basiques carbonatés et silicatés - Détermination de la réactivité - Méthode par titrage potentiométrique à l'acide chlorhydrique

Carbonatische und silikatische Kalke - Bestimmung der Reaktivität - Potentiometrisches Titrationsverfahren mit Salzsäure

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

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European foreword

This document (prEN 13971:2019) 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 CEN Enquiry.

This document will supersede EN 13971:2012.

The following changes have been made to the former edition:

a) Clause 1, Scope enlarged by adding an indication of the special sample preparation for liming materials coarser than 1 mm;

b) Clause 11, Test report enlarged by adding a requirement on confirmation that partical size proportional weighing of the test sample was performed according to Annex A;

c) Clause 3, Terms and definitions editorially revised;

d) Clause 10, Precision editorially revised.

Introduction

The results obtained by this method can be used to estimate the behaviour of the liming material in the soil. The results show a good correlation with the results obtained by a soil incubation method (see [1] to [5]). Regarding the precision of the method, the results are not used to declare a value, but to classify the different product groups.

1 Scope

This document specifies a method for the determination of the speed and effectiveness of the neutralizing potential of calcium carbonate, calcium magnesium carbonate and calcium magnesium silicate liming materials by potentiometric titration with hydrochloric acid.

For liming materials coarser than 1 mm, it is essential to prepare the sample of a liming material by following exactly the description of Annex A.

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

The type of liming material can be identified according to EN 14069 and the particle size can be determined according to EN 12948.

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.

prEN ISO 14820-2, *Fertilizers and liming materials — Sampling and sample preparation — Part 2: Sample preparation (ISO 14820-2)*

EN 12048, *Solid fertilizers and liming materials — Determination of moisture content — Gravimetric method by drying at (105 ± 2) °C (ISO 8190:1992 modified)*

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

EN 12947, *Liming materials — Determination of magnesium content — Atomic absorption spectrometric method*

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

EN 13475, *Liming materials — Determination of calcium content — Oxalate method*

3 Terms and definitions

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

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

- IEC Electropedia: available at http://www.electropedia.org/
- ISO Online browsing platform: available at http://www.iso.org/obp

4 Principle

Decomposition of carbonates and silicates with acids according to the following reactions:

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

$MeSiO_4 + 2\ H^+ \rightarrow Me(OH)_2 + SiO_2$

Titration under stable pH conditions either with an automatic titration apparatus or a manual method. The acid consumption during a given time is a direct measure of the reaction rate of the liming materials being tested.

5 Apparatus

Usual laboratory apparatus and, in particular, the following:

5.1 pH meter, with electrode.

5.2 Burette.

NOTE Used only for 5,0 mol/l hydrochloric acid solution (6.2).

5.2.1 50 ml motor driven burette, for automatic titration.

A pH stat function is recommended, for example Metrohm 716 DMS Titrino®[1)].

5.2.2 50 ml burette, for manual titration.

5.3 250 ml glass beaker, with an inner diameter of 65 mm.

5.4 Magnetic stirrer, with centring mark for the 250 ml glass beaker.

5.5 Magnetic stirrer rod, (9 ± 1) mm diameter times (50 ± 1) mm length, with central ring.

5.6 Stop-watch.

5.7 Filter paper, acid-proof, medium filtration speed, average retention capacity about 5 µm to 12 µm.

6 Reagents

All reagents shall be of recognized analytical grade.

6.1 Hydrochloric acid solution, mass fraction, $w(HCl)$ = 25 %.

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

6.3 Calcium carbonate, precipitated, mass fraction, $w(CaCO_3)$ = of at least 99 %.

Precipitated calcium carbonate is from crystalline origin. Commercial PCC for analysis is granted for its chemical characteristics. However, physical characteristics are not granted. The use of a highly reactive PCC, such as commercial PCC from VWR / Prolabo / BDH, reference GPR, Rectapur, Ref 22296.294, Molar mass 100,09[2)] which will consume 15 ml after 15 min, is recommended.

6.4 Silicone defoamer.

6.5 Standard buffer solution, pH = 2,0, commercial solution.

NOTE This has a limited life.

6.6 Standard buffer solution, pH = 4,0, commercial solution.

NOTE This has a limited life.

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1) Metrohm 716 DMS Titrino® 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. Equivalent products may be used if they can be shown to lead to the same results.

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

7 Preparation of the test sample

7.1 Prepare the sample of the liming material in accordance with prEN ISO 14820-2.

7.2 Dry the test sample in accordance with EN 12048. Record the result for information only.

7.3 Use the dried test sample without further preparation, e.g. grinding.

7.4 Weigh a 5,0 g test portion of the dried sample to the nearest 0,01 g. For liming materials coarser than 1 mm, the test portion shall be prepared in accordance with Annex A.

8 Procedure

8.1 Automatic titration

8.1.1 Calibration

8.1.1.1 Calibrate the pH meter (5.1) with two standard buffer solutions, pH 2,0 (6.5) and pH 4,0 (6.6) to exactly the indicated values. The pH electrode shall react quickly.

Check the sluggishness of the electrode and if necessary, clean it carefully with hydrochloric acid (6.1) and re-calibrate with the standard buffer solutions.

Checking and cleaning is more frequently required for liming materials containing clay.

It is recommended to flush the acid introduction pipe between each sample for slow reacting samples.

8.1.1.2 Adjust the motor driven burette (5.2.1) to the position “continuous working” and a standard flow rate of 35 ml/min to 38 ml/min.

NOTE Wide deviations in the flow rate adversely affect the results obtained.

8.1.1.3 Place the glass beaker (5.3) centrally on the magnetic stirrer (5.4). Add 100 ml water and the magnetic stirrer rod (5.5). The test apparatus shall be arranged according to Figures B.1 and B.2.

8.1.1.4 Set the magnetic stirrer speed control to between 500 min^{-1} and 600 min^{-1}. Fill the burette (5.2.1) with 5,0 mol/l hydrochloric acid (6.2).

8.1.1.5 Adjust the titration control so that the stepwise run of the titration only starts below pH 2,5. For apparatus with a step length adjustment, set the adjustment at the middle position.

8.1.1.6 Set up the electrode (5.1) and the burette (5.2.1) in the glass beaker (5.3) according to Figures B.1 and B.2. This is to ensure that the added hydrochloric acid (6.2) is mixed with the contents of the glass beaker before reaching the electrode (5.1). Avoid contact with the walls of the glass beaker.

8.1.1.7 For the exact adjustment of the operating conditions, start the magnetic stirrer (5.4) and add (5,00 ± 0,01) g of calcium carbonate (6.3) to the stirred water in the glass beaker (5.3). The solution should be stirred for 30 s. Start the stop-watch (5.6) and commence the titration, adding the hydrochloric acid (6.2) in a fast sequence of drops, aiming at a pH value of 2,0.

When pH 2,5 is reached, add the hydrochloric acid more slowly. Use (16 ± 0,2) ml of hydrochloric acid in the first 30 s and then continue with stepwise additions to dissolve the remaining carbonate within 60 s. Check the acid consumption is (20,0 ± 0,2) ml of 5,0 mol/l hydrochloric acid (6.2). During the procedure the solution shall not be allowed to fall below pH 2,0 by more than 0,2 pH units, even for a short time.

If the material being tested foams very strongly, one drop of silicon defoamer (6.4) should be added to the solution.

When operating conditions are correctly adjusted, about 80 % of the mass of calcium carbonate is dissolved by the first 16 ml of hydrochloric acid (6.2) which should run almost uninterrupted. The remaining amount of calcium carbonate should be dissolved by a further 4 ml of hydrochloric acid, added stepwise, within the next 60 s. Any fine adjustment that might be necessary can be carried out by a slight alteration to the start of the stepwise titration or by changing the length of the titration.

A pH stat function is recommended for the titration.

8.1.2 Determination

8.1.2.1 Set up the apparatus as described in 8.1.1.1 to 8.1.1.6.

8.1.2.2 Add the weighed test portion (7.4) to the stirred water in the glass beaker (5.3) and immediately start the stop-watch (5.6) and the titration procedure. The possible abrasive effect of stirring is reduced by commencing the titration immediately the magnetic stirrer (5.4) is switched on.

8.1.2.3 Stop the titration after 10 min and record the amount of acid consumed. During the procedure the pH value shall not be allowed to fall below pH 2,0 by more than 0,2 pH units, even for a short time. For carbonate liming materials continue with 8.1.

8.1.2.4 For silicate liming materials immediately after end of titration pass the suspension through a dry filter (5.7) into a dry container without rinsing the pH electrode. Discard the initial portion. Take an aliquot portion and dilute it with water to a measurable concentration (e.g. 1:100). Determine the concentration of calcium and in the solution according to EN 13475 and magnesium according to EN 12947. Repeat the titration three times. Take the mean acid consumption of the four titrations and record this amount.

8.2 Manual titration

8.2.1 Calibration

8.2.1.1 Calibrate the pH meter (5.1) with two standard buffer solutions, pH 2,0 (6.5) and pH 4,0 (6.6) to exactly the indicated values. The pH electrode shall react quickly.

Check the sluggishness of the electrode and if necessary, clean it carefully with hydrochloric acid solution (6.1) and re-calibrate with the standard buffer solutions (see 8.1.1.1).

8.2.1.2 Place the glass beaker (5.3) centrally on the magnetic stirrer (5.4). Add 100 ml water and the magnetic stirrer rod (5.5).

8.2.1.3 Set the magnetic stirrer speed control to between 500 min^{-1} and 600 min^{-1}. Fill the burette (5.2.2) with 5,0 mol/l hydrochloric acid (6.2).

8.2.1.4 Set up the electrode (5.1) and the burette (5.2.2) in the glass beaker (5.3) according to Figures B.1 and B.2. This is to ensure that the added hydrochloric acid (6.2) is mixed with the contents of the glass beaker before reaching the electrode (5.1). Avoid contact with the walls of the glass beaker.

8.2.1.5 For the exact adjustment of the operating conditions, start the magnetic stirrer (5.4) and add (5,00 ± 0,01) g of calcium carbonate (6.3) to the stirred water in the glass beaker (5.3). Start the stop-watch (5.6) and commence the titration, adding the hydrochloric acid (6.2) in a fast sequence of drops, aiming at a pH value of 2,0.