# SLOVENSKI STANDARD

**SIST EN 13971:2003**

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**Karbonatni materiali za apnjenje – Ugotavljanje reaktivnosti – Potenciometrijska titracijska metoda s solno kislino**

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

Carbonatische Kalke - Bestimmung der Reaktivität - Potentiometrisches Titrationsverfahren mit Salzsäure



Amendements minéraux basiques carbonatés - Détermination de la réactivité - Méthode par titration potentiométrique a l'acide chlorhydrique



**Ta slovenski standard je istoveten z: EN 13971:2002**

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

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

Carbonatische 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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# Contents

## Foreword

This document (EN 13971:2002) 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of an identical text or by endorsement, at the latest by June 2003, and conflicting national standards shall be withdrawn at the latest by June 2003.

Annexes A and B are normative.

This document contains a Bibliography.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Malta, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom.

# 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]).

## 1 Scope

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

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

NOTE In addition, the type of liming material should be identified according to prEN 14069.

Regarding the precision of the method, the results are not used to declare a value but to classify the different products groups.



## 2 Normative references

This European Standard incorporates by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text, and the publications are listed hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this European Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies (including amendments).

EN 1482, *Sampling of solid fertilizers and liming materials.*

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

ISO 5725:1986[1)], *Precision of test methods — Determination of repeatability and reproducibility for a standard test method by inter-laboratory tests.*

## 3 Principle

Decomposition of carbonates with acids according to the following reaction:

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

1) ISO 5725:1986 (now withdrawn) was used to obtain the precision data.

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 for the reaction rate of the liming materials being tested.

## 4 Apparatus

Usual laboratory apparatus and, in particular, the following.

**4.1 pH meter**with electrode.

**4.2 Burette**

NOTE Use only for 5,0 mol/l hydrochloric acid solution (5.3).

**4.2.1 50 ml motor driven burette** (for automatic titration), for example Metrohm 716 DMS Titrino® 2)

**4.2.2 50 ml burette** (for manual titration)

**4.3 250 ml glass beaker,** with an inner diameter of 65 mm.

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

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



**4.6 Stop-watch**



## 5 Reagents

**5.1 General**

All reagents shall be of recognized analytical grade.

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

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

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

**5.5 Silicone defoamer**

**5.6 Standard buffer solution, pH 2,0** (commercial solution).

NOTE This has a limited life.

**5.7 Standard buffer solution, pH 4,0** (commercial solution).

NOTE This has a limited life.

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2) 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.

## 6 Preparation of the test sample

**6.1** Sample the liming material in accordance with EN 1482.

**6.2** Dry test sample in accordance with EN 12048. Record the result.

**6.3** Use test sample without further preparation, e.g. grinding.

**6.4** Weigh out a 5,0 g test portion to the nearest 0,01 g. For liming materials coarser than 1 mm, the test portion should be prepared in accordance with annex A.

## 7 Procedure

### 7.1 Automatic titration

#### 7.1.1 Calibration

**7.1.1.1** Calibrate the pH meter (4.1) with two standard buffer solutions, pH 2,0 (5.6) and pH 4,0 (5.7) 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 with a mass fraction of 25 % (5.2) and re-calibrate with the standard buffer solutions.

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



**7.1.1.2** Adjust the motor driven burette (4.2.1) 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.

**7.1.1.3** Place the glass beaker (4.3) centrally on the magnetic stirrer (4.4). Add 100 ml water and the magnetic stirrer rod (4.5).

**7.1.1.4** Set the magnetic stirrer speed control to between 500 $min^{-1}$ and 600 $min^{-1}$. Fill the burette (4.2.1) with 5,0 mol/l hydrochloric acid (5.3).

**7.1.1.5** 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.

**7.1.1.6** Set up the electrode (4.1) and the burette (4.2.1) in the glass beaker (4.3) according to Figures B.1 and B.2. This is to ensure that the added hydrochloric acid (5.3) is mixed with the contents of the glass beaker before reaching the electrode (4.1). Avoid contact with the walls of the glass beaker.

**7.1.1.7** For the exact adjustment of the operating conditions, start the magnetic stirrer (4.4) and add (5,00 ± 0,01) g of calcium carbonate (5.4) to the stirred water in the glass beaker (4.3). Start the stop-watch (4.6) and commence the titration, adding the hydrochloric acid (5.3) in a fast sequence of drops, aiming at a pH value of 2,0.

When pH 2,5 is reached, the hydrochloric acid shall be added more slowly. Use (16 ± 0,2) ml to convert about 80 % of the carbonate within the first 30 s. Within a further 60 s the remaining carbonate should be dissolved. Check that the acid consumption is (20,0 ± 0,2) ml of 5,0 mol/l hydrochloric acid (5.3). 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.

NOTE 1 If the material being tested foams very strongly, one drop of silicon defoamer (5.5) should be added to the solution.

NOTE 2 When correctly adjusted, about 80 % of the given amount of calcium carbonate will have been dissolved in the first 30 s using about 16 ml of hydrochloric acid (5.3). During this phase, the acid supply should run practically uninterrupted. Only then should the step-wise run of the titration start, and the remaining amount of the calcium carbonate should be dissolved

using about a further 4 ml of hydrochloric acid (5.3) and taking some 60 s more. A corresponding fine comparison can be carried out by slightly changing the start of the step-wise titration or by changing the length of the titration. It should be checked that the acid consumption is (20 ± 0,2) ml of 5,0 mol/l hydrochloric acid (5.3).

#### 7.1.2 Determination

**7.1.2.1** Set up the apparatus as described in 7.1.1.1 to 7.1.1.6.

**7.1.2.2** Add the weighed test portion (6.4) to the stirred water in the glass beaker (4.3) and immediately start the stop-watch (4.6) and the titration procedure. The possible abrasive effect of stirring is reduced by commencing the titration immediately the magnetic stirrer (4.4) is switched on.

**7.1.2.3** Stop the titration after 10 min and record the amount of acid consumed. During the procedure the pH shall not be allowed to fall below pH 2,0 by more than 0,2 pH units, even for a short time.

**7.1.2.4** Repeat the titration three times. Take the mean acid consumption of the four titrations and record this amount of 5,0 mol/l hydrochloric acid (5.3) used.

### 7.2 Manual titration

#### 7.2.1 Calibration

**7.2.1.1** Calibrate the pH meter (4.1) with two standard buffer solutions, pH 2,0 (5.6) and pH 4,0 (5.7) 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 with a mass fraction of 25 % (5.2) and re-calibrate with the standard buffer solutions (see note in 7.1.1.1).



**7.2.1.2** Place the glass beaker (4.3) centrally on the magnetic stirrer (4.4). Add 100 ml water and the magnetic stirrer rod (4.5).



**7.2.1.3** Set the magnetic stirrer speed control to between 500 $min^{-1}$ and 600 $min^{-1}$. Fill the burette (4.2.2) with 5,0 mol/l hydrochloric acid (5.3).

**7.2.1.4** Set up the electrode (4.1) and the burette (4.2.2) in the glass beaker (4.3) according to Figures B.1 and B.2. This is to ensure that the added hydrochloric acid (5.3) is mixed with the contents of the glass beaker before reaching the electrode (4.1). Avoid contact with the walls of the glass beaker.

**7.2.1.5** For the exact adjustment of the operating conditions, start the magnetic stirrer (4.4) and add (5,00 ± 0,01) g of calcium carbonate (5.4) to the stirred water in the glass beaker (4.3). Start the stop-watch (4.6) and commence the titration, adding the hydrochloric acid (5.3) in a fast sequence of drops, aiming at a pH value of 2,0.

When pH 2,5 is reached, the hydrochloric acid shall be added more slowly. Use (16 ± 0,2) ml to convert about 80 % of the carbonate within the first 30 s. Within a further 60 s the remaining carbonate should be dissolved. Check that the acid consumption is (20,0 ± 0,2) ml of 5,0 mol/l hydrochloric acid (5.3). 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.

#### 7.2.2 Determination

**7.2.2.1** Set up the apparatus as described in 7.2.1.1 to 7.2.1.3.

**7.2.2.2** Add the weighed test portion (6.4) to the stirred water in the glass beaker (4.3) and immediately start the stop-watch (4.6) and the titration procedure. The possible abrasive effect of stirring is reduced by commencing the titration immediately the magnetic stirrer (4.4) is switched on.

**7.2.2.3** Add the hydrochloric acid (5.3) in a fast sequence of drops, aiming at a pH of 2,0. Do not allow the pH to drop below 2,0.