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

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

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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This document was prepared by the European Committee for Standardization (CEN) (as EN 16357/2013) and was adopted, without modification apart from editorial corrections, by Technical Committee ISO/TC 134, *Fertilizers, soil conditioners and beneficial substances*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

This document has been prepared to improve the existing agricultural reactivity methods (see References [8], [9], [10], [11] and [12]) for carbonate liming materials: duration, accuracy, representativeness, closer from soil conditions, automation.

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

1 Scope

This document specifies a method for determining 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 in accordance with ISO 20977.

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

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.

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

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

ISO 20977, *Liming materials — Determination of size distribution by dry and wet sieving*

ISO 20978, *Liming materials — Determination of neutralizing value — Titrimetric methods*

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

3 Terms and definitions

No terms and definitions are listed in this document.

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

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

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

4 Principle

The principle of the method is based on the following points:

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

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

where Me represents Ca, Mg, etc;

— 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.

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 the accuracy of added amounts of citric acid solution);

— suitability of precipitated calcium carbonate (PCC) used to check calibration;

— stirring device (provides homogeneousness without grinding);

— additional uncertainty with neutralising value and MgO content determination.

5 Apparatus

The usual laboratory apparatus and, in particular, the following:

5.1 pH meter with electrode.

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

5.2 Automatic motor-driven burette, with a capacity of 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 (5.7) may be used, provided the central ring of the stirring rod is thick enough and does not lead to the grinding of the tested material. Make sure the rotation speed of the stirring rod is fast enough to make a homogeneous dispersion in the beaker. If not, increase the speed up to the appropriate value.

The burette shall deliver at least 0,05 ml/s of citric acid solution (6.3). This is to ensure the first part of the reaction [pH dropping from initial pH value to target pH value (4,5) is not 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 deliver its whole content in at least 4 000 steps to ensure accuracy for small amounts of citric acid solution (6.3).

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

Use the burette only for the citric acid solution (6.3).

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

For most products, a 10 ml burette is sufficient. However, a 20 ml burette is necessary for highly reactive chalks and precipitated calcium carbonate (PCC). Because refilling takes a significant amount of time, this can alter 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.

5.3 Glass beaker, with a capacity of 100 ml.

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

Minimum diameter in case of magnetic stirring device (5.7): 50 mm.

5.4 Stop-watch.

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

5.6 Sample changer, optional.

If a sample changer is utilized, a beaker of water (6.1) shall be inserted between two samples.

5.7 Magnetic stirring device, optional, (see 5.2).

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

Stirring rod minimum length: 40 mm.

6 Reagents

All reagents shall be of recognized analytical grade.

6.1 Water, meeting the requirements of ISO 3696, grade 2.

6.2 Citric acid monohydrate, $C_6H_8O_7\ H_2O$, crystallized or powdered, molar mass: 210,14 g/mol.

Do not use anhydrous citric acid having a different molar mass and can partially hydrate when stored.

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

Preferably, use a fresh home-made solution as described below. Its pure citric acid concentration is conventionally supposed to be the required one, i.e. ρ_{ca} = 457,17 g/l.

The solution may be used for up to one month if stored in a closed, dark glass vessel. If the solution has been stored for 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 Formula (2).

Weigh 500 g of citric acid monohydrate (6.2) 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 (6.1) to the measuring vessel. Heat the vessel until full dissolution (at a temperature of about 80 °C). Let the vessel cool to ambient temperature. Make up the volume with water to 1 l. Stir to get a homogeneous solution.

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

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

where

500 is the added mass of citric acid monohydrate (6.2), in grams (g);

192,14 is the molar mass of anhydrous citric acid, in grams per mole (g/mol);

210,14 is the molar mass of citric acid monohydrate, in grams per mole (g/mol).

6.4 Calcium carbonate, precipitated (PCC), with a mass fraction $w(CaCO_3)$ of at least 99 %.

Commercial PCC for analysis is certified for its chemical characteristics. However, its physical characteristics are not certified. As reactivity depends on fineness, even for PCC, it is essential to take a highly reactive PCC[1)] as a reference, which consumes 15 ml in 15 min. This type of PCC was used in the ring test before launching measurements. By experience, some types of PCC do not meet this requirement. See also the note in 8.2.6.

6.5 Silicone defoamer.

6.6 Standard buffer solution, pH = 4 (commercial solution, pH = 4,01).

NOTE This solution has a limited lifetime.

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

NOTE This solution has a limited lifetime.

7 Sampling and sample preparation

7.1 General

Sampling is not part of the methods specified in this document. A recommended sampling method is given in ISO 14820-1.

Sample preparation shall be carried out in accordance with ISO 14820-2.

This document specifies that samples are tested “as received” in order to allow immediate starting of all the necessary measurements (Neutralizing Value, MgO). No preliminary determination is required to calculate the mass of the tested samples. However, make sure that sample moisture is the same in the reactivity test portion as in the neutralising value measurement.

Correcting factors are to be applied later on in the expression of results: actual citric acid concentration, exact mass of sample, as received neutralising value, MgO content. Such a procedure shortens the total necessary time for analysis because required measurements are made simultaneously instead of successively. However, the additional uncertainty introduced by the correction factors is neither described in this document nor taken into account for the precision data mentioned in Clause 10. All implemented correction factors should be evaluated to quantify the additional uncertainty they introduce to the expression of the reactivity.

NOTE This procedure is also better than drying the sample before titrating, because drying can modify fineness or physical presentation and consequently have an impact on the reactivity of some products.

1) Such as commercial PCC from VWR / BDH Prolabo ®, GPR, Rectapur®, Ref 22296.294, Molar mass 100,09. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

7.2 Preparation of the test sample

Measure the moisture content of the tested material in accordance with EN 12048 and record the result for information.

Make sure there is no oxide or hydroxide in the material to be tested (pH with 1/10 dilution shall be below 10). An oxide or hydroxide fraction in the product alters the result. Oxide or hydroxide chemical forms are not included in the scope of this method.

Use the test sample without any further preparation, e.g. grinding or drying.

NOTE The procedure (8.3.2) includes a fixed time of preliminary stirring.

7.3 Preparation of the test portion

Weigh (5,0 ± 0,2) g of the test sample as received to the nearest 0,01 g and record the weight.

For liming materials coarser than 1 mm, or which appear to be heterogeneous, the test portion shall be prepared by fraction sampling in accordance with Annex A, and a test portion of 10 g shall be taken instead of 5 g. This can happen even if the material particle size is finer than 1 mm. The representativeness of the product as delivered in the 5 g or 10 g test portion is the most important aspect.

Note that fraction sampling involves additional uncertainty. Consequently, it should be used only if the coarse particles are higher than 4 mm. Otherwise, increase the test portion up to 10 g.

8 Procedure

8.1 General

The determination shall be made under usual laboratory conditions, i.e. ambient temperature [(20 ± 2) °C].

Reagents shall be at the same room temperature.

As this method does not use a total reaction but a partial one in a limited amount of time, the accuracy of results is highly dependent on trained and skilled staff. Do not proceed to perform measurements until the analyst becomes familiar with the method.

8.2 Calibrations

8.2.1 Calibrate the pH meter (5.1 or 5.2) with two buffer solutions, pH = 4 (6.6) and pH = 7 (6.7), to exactly the indicated values before each series of measurement. The pH electrode shall react quickly. Check that it can change from pH 4 to pH 7 within 5 s.

Check the sluggishness of the electrode and, if necessary, clean it carefully with the citric acid solution (6.3) and re-calibrate with the standard buffer solutions.

If the pH regulation system only accepts mV instead of pH for the target value, register mV values during calibration at pH 4 and pH 7 and calculate by interpolation the mV value corresponding to a pH target value of 4,5.

This mV value can vary over time for the same pH electrode.

This value shall be calculated each time a new series is being processed, just after calibration.

Checking and cleaning shall be more frequent for liming materials containing clay.